

ON THE MOLECULAR THEORIES OF
LIQUID CRYSTALS

by

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Dottore in Chimica Industriale

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ABSTRACT

FACULTY OF SCIENCE

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ON THE MOLECULAR THEORIES OF LIQUID CRYSTALS

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This thesis is concerned with the statistical theory of liquid crystals and the molecular reorientation in these anisotropic fluids.

The first chapter reviews the definition and the experimental determination of the order parameters. We then develop, in the second chapter, a statistical theory of the nematic mesophase, starting from the total partition function for rod-like particles and arriving at an effective orientational partition function. The usual molecular field theory of nematics is obtained as the first term in a rather general expansion. An extension of the molecular field theory to uniaxial nematics formed by non-cylindrically symmetric molecules is discussed in Chapter 3 and comparison is made with available experimental data.

The study of molecular reorientation in such anisotropic systems as liquid crystals or membranes by using electron resonance is the subject of the remainder of the thesis. In Chapter 4 some background material on spin relaxation and the theory of reorientation in the presence of an ordering potential is reviewed. Methods for the computation of the spectral densities are also developed. The molecular reorientation of a monoradical spin probe in a highly ordered smectic A phase is studied in

Chapter 5 by analyzing the angular dependence of the electron resonance linewidths in terms of both a strong collision and a diffusion model. The determination of the order parameter $\bar{P}_4$ is discussed. The spin relaxation theory employed is generalized in Chapter 6 to include the effect on the angular dependent linewidths of the pseudosecular terms in the static spin hamiltonian. The predictions of this theory are illustrated with model calculations. Finally, in Chapter 7 a theory is developed, and experimental data analyzed, for the angular dependence of the spectral linewidths of biradical spin probes.

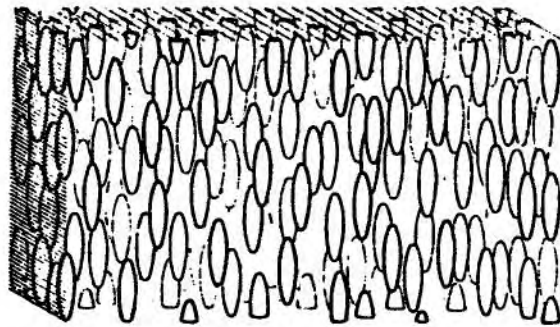
CHAPTER ONE

ORIENTATIONAL ORDER IN LIQUID CRYSTALS

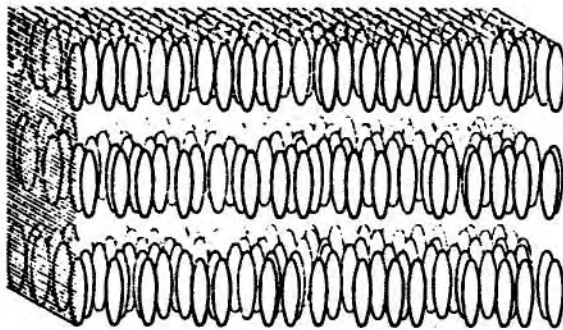
1.1 Liquid Crystals

A liquid crystal is an equilibrium phase intermediate between a liquid and a crystal. At a microscopic level crystals formed of non-spherical molecules are characterized by a long-range order both in the position and the orientation of their constituents and normal liquids by the absence of both. In contrast a liquid-crystalline phase, often called a mesophase, can still possess an orientational order, while the positional one is greatly reduced or absent altogether (1,2). More precisely, the amount of positional order helps to classify liquid crystals into various types: nematics and cholesterics having no positional order, and smectics having the molecular centres of mass arranged in layers (3). An idealized diagram of the molecular organization of nematics, cholesterics, and smectics is pictured in figure 1.1. The common feature in all these three types, as well as in the various subtypes, is the existence of a preferred or average molecular orientation, called the director.

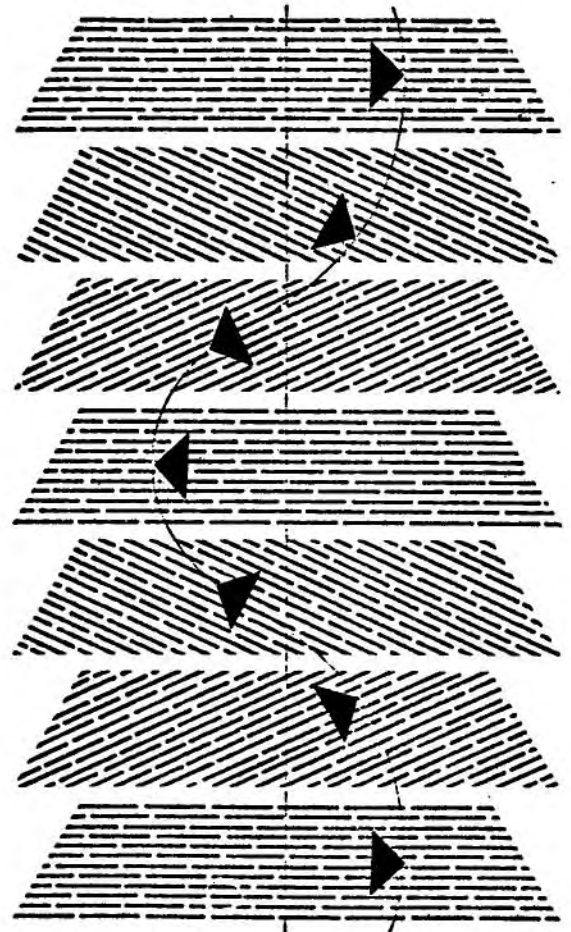
Liquid-crystalline phases can be produced in two basic ways: either by dissolving the mesogen in an appropriate solvent or by a thermal transition. Substances giving mesophases in just the first way are called lyotropics (4), an example being soaps; the others are termed thermotropics (5,6). We shall be only concerned with the latter type in this thesis, even if many of our arguments, *mutatis mutandis*, could be applied to lyotropics as well.



a



b



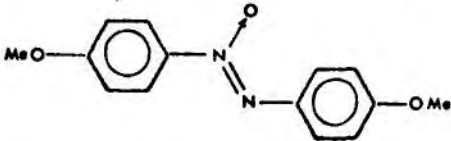
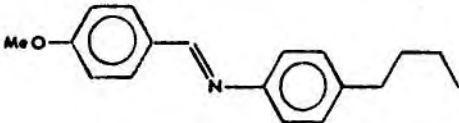
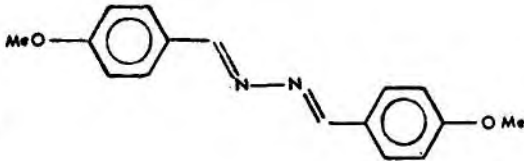
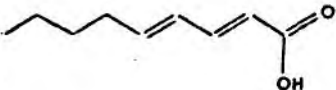
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Figure 1.1 Molecular organisation in (a) the nematic phase, (b) smectic phase, and (c) the cholesteric phase.

A typical example of a thermotropic nematic liquid crystal is 4,4'-dimethoxyazobenzene. This is crystalline at room temperature and gives on melting a turbid phase which on further heating yields an ordinary, clear, liquid. The mesophase owes its characteristic turbid appearance to the fact that the director changes continuously orientation from one point of the sample to the other, to preserve the spherical symmetry of the isotropic phase, and the resulting orientational inhomogeneity causes light scattering (1,2). This full rotational symmetry of the nematic mesophase is easily broken. For example the director can be readily oriented by applying a magnetic field (7), because of the enhancement of the anisotropy in the susceptibility caused by the orientational correlation. The result is that the motion of every single molecule with respect to the director is relatively unaffected by the field, but the liquid crystal as a whole is aligned (2,8). The oriented mesophase is an unusual state of matter in that it has, as an example, the optical and dielectric properties of a uniaxial crystal, the director being the axis of symmetry, while still retaining the mobility of a fluid. In a sense it is then an anisotropic fluid. Much of both the theoretical interest and of the practical applications of liquid crystals (9,10,11) stem from this fact together with their ease of alignment by magnetic and electric fields (12) as well as properly treated surfaces (13).

From a chemical point of view the molecules of mesogens, i.e. substances giving rise to liquid crystalline phases, can be quite simple and it is estimated that, on average, one out of two hundred of organic molecules has this property. To give some examples we have listed in Table 1.1 the structure and the transition temperatures of some

TABLE 1.1 The structure and the transition temperature of some nematogens.

NAME AND FORMULA	$T_{\text{solid-nem.}}/^{\circ}\text{C}$	$T_{\text{nem.-isotropic}}/^{\circ}\text{C}$	Ref.
1) 4,4'-dimethoxyazoxybenzene (PAA)	118	136	14
			
2) 4-methoxybenzylidene-4'-n-butylaniline	22	48	15
			
3) anisaldazine	169	184	14
			
4) 2,4-nonadienic acid	23	49	14
			
5) p-quinquephenyl	401	445	14
			

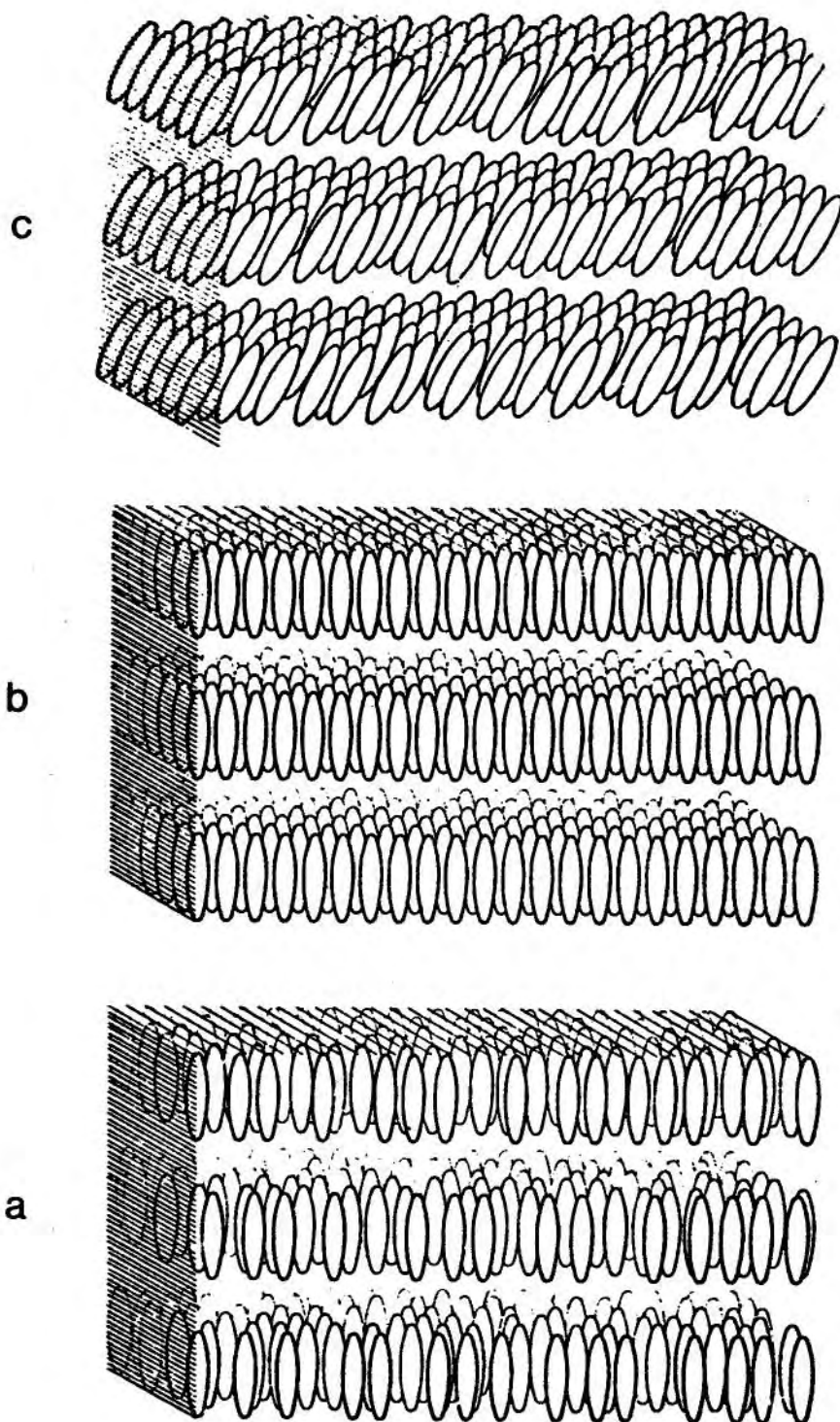
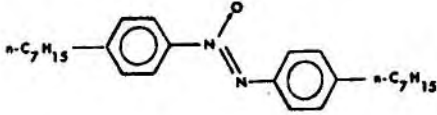
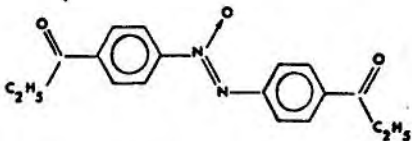
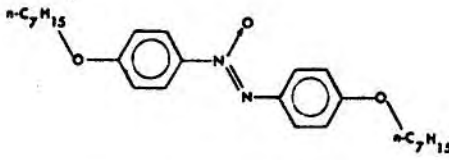
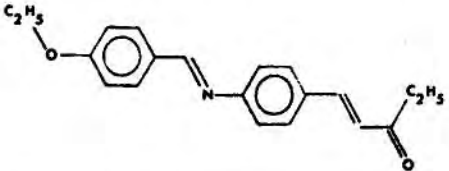
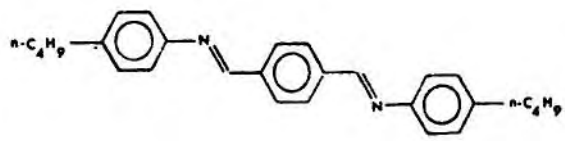


Figure 1.2 The molecular organisation in (a) the smectic A phase, (b) untilted smectic B phase and (c) the smectic C phase.

TABLE 1.2 The transition temperatures of some smectogens (a)

Name and formula	Temperatures (°C) for the transition to					Ref.
	S _B	S _C	S _A	N	I	
4,4'-di(n-heptyl)azoxybenzene 			34	54	71	23
Diethyl 4,4'-azoxybenzdicarboxylate 			114		122.6	6
4,4'-di-n-heptyloxyazoxybenzene 		74		94	124	6
Ethyl 4-ethoxybenzylidene-4'-aminocinnamate 	81.7		118.5	156.5	159	6
Terephthal-bis (butylaniline) 	113	144	172	200	236	1

(a) S_A, S_B, S_C, indicate the smectic A, B, C types; N and I indicate the nematic and isotropic phase.

The first number from the left of every entry is the transition temperature from the solid.

typical nematics. Common features are a high length to breadth ratio, rigidity, and anisotropy in the polarizability tensor, usually ensured by conjugated π electron systems. They often contain permanent dipoles but these are not essential for the formation of the mesophase, as proved by the existence of virtually apolar mesogens (e.g. the last entry in Table 1.1) and from the fact that liquid crystals do not exhibit the ferroelectricity expected if dipole-dipole interactions were important.

Nematogens, in particular, are not optically active. If the molecule is chiral, then the hypothetical mesophase produced will be cholesteric, i.e. a naturally twisted version of nematics having the director wound in a helical shape, with a pitch of typically about 2000 Å (1,16,17).

Molecules giving smectics, i.e. layered liquid crystals, have again the same general characteristics but moreover they usually have flexible alkyl chains at the ends and strong dipole moments more or less perpendicular to the central part. The different ordering of these dipoles in the smectic layer has been invoked (18,19) as a possible explanation of the existence of many different smectic types (20,21,22). In figure 1.2 we illustrate three of these types, the smectic A, B and C. Notice that the preferred orientation is perpendicular to the layer in the A type and tilted with respect to it in the C type. The smectic B, in contrast with the other two types, possesses some degree of spatial order inside each layer. The director can be parallel or tilted to the layer normal in analogy with smectic A and C types. The structure and transition temperatures of some smectogens are listed in Table 1.2.

To describe a liquid crystal two concepts are particularly relevant: that of a director and of a set of order parameters.

The director is a unit vector defined at every point of the sample and giving the local preferred orientation. It is assumed to vary slowly and continuously from one point to another except in certain regions called disclinations, where the preferred orientation changes abruptly (1,24). The concept of the director is a macroscopic one, even though it can be given a molecular statistical definition, and a continuum theory of liquid crystals has been developed (1,24-29) which describes the behaviour of nematics under external perturbations in terms of the deformation energy of the director field. Typical examples are the determination of the equilibrium conformation of a nematic under certain boundary conditions or in the presence of an electric or magnetic field, the study of its flow and surface properties etc... While successful in explaining such effects, the continuum theories give no direct information on the behaviour of liquid crystals at a molecular level, which is our major concern in this thesis.

From a molecular point of view we shall find it particularly useful to introduce a set of orientational order parameters describing to what extent the molecules align with respect to the director. The importance of the concept of an order parameter in studying phase transitions is well known (30). In general it can be defined as a quantity (or a set of quantities) which is non zero below a certain critical temperature T_k , and zero above it. As an example, for the common liquid-gas transition the order parameter can be taken as the difference between the density of the gas and the liquid $\rho_G - \rho_L$ and for a ferromagnetic system it can be taken as the magnetization, which

again vanishes above a certain temperature, the Curie point. The way the order parameter changes in the course of a phase transition is also important since it tells us something about the character of the transition; a discontinuity indicates a first order phase transition while a continuous change indicates a second order one. The first type is also characterized of course by a discontinuity in the first derivative of an appropriate thermodynamical potential (the Gibbs free energy, say) and the other by a discontinuity or an infinity in the second order derivative of this potential.

In the rest of this first chapter we shall treat in some detail the set of order parameters relevant for the description of liquid crystals. In Section 1.2 this set is defined in a general way and then specialized to the important case of uniaxial mesophases composed of cylindrically symmetric molecules. The way the order parameters can be determined experimentally is then discussed in Section 1.3.

•

1.2 The Orientational Order Parameters

It is usually assumed that the orientational order in uniaxial liquid crystals is the average of just the second Legendre polynomial: $\overline{P}_2 = (3\cos^2\beta - 1)/2$, where β is the angle between the axis of symmetry of the molecule, assumed to be rodlike, and that of the mesophase. The upper bar denotes an ensemble average (31,32). The argument for this choice is that $\overline{P}_2$ obviously reduces to the proper limits: $\overline{P}_2 = 0$ in the case of no alignment, i.e. an isotropic system, and $\overline{P}_2 = 1$ in the case of a perfect alignment. However, Humphries, James and Luckhurst (33) have shown that in the molecular field limit one should more properly have not just one, but an infinite set of order parameters, given by the ensemble averages of all the Legendre polynomials:

$$\overline{P}_2, \overline{P}_4, \overline{P}_6, \dots$$

In this section we shall define a set of orientational order parameters in a general way i.e. as the minimal set of quantities necessary to describe completely the singlet orientational distribution function $f(\alpha\beta\gamma)$. This distribution is defined as the probability density that the orientation of a molecule is given by the three Euler angles $(\alpha\beta\gamma)$ (34). The ensemble average of any single particle orientational function $A(\alpha\beta\gamma)$ can be expressed in terms of $f(\alpha\beta\gamma)$ as

$$\overline{A} = \int A(\alpha\beta\gamma) f(\alpha\beta\gamma) d\alpha \sin\beta d\beta d\gamma. \quad (1.1)$$

As any other well behaved function of three Euler angles the singlet distribution can be expanded in a basis of Wigner rotation matrices

$$D_{m,n}^L(\alpha\beta\gamma) \text{ as}$$

$$f(\alpha\beta\gamma) = \sum C_{Lmm} D_{m,n}^L(\alpha\beta\gamma). \quad (1.2)$$

The definition and the main properties of the Wigner rotation matrices are described in Appendix 1. Multiplying both sides of equation (1.2) by $D_{m,n}^{L*}$ and integrating over the angles, we find,

$$C_{Lmm} = \frac{2L+1}{8\pi^2} \overline{D_{m,n}^{L*}}. \quad (1.3)$$

because of the orthogonality of Wigner matrices. The averages $\overline{D_{m,n}^L}$ are our set of order parameters (35,36). The expansion can be simplified using the symmetry property of the mesophase or of the constituent particles. For uniaxial phases, as the nematic or smectic A are found to be, the singlet distribution must be invariant under rotation about the z axis if this is chosen along the director i.e. the axis of symmetry. This implies that m must be zero in $\overline{D_{m,n}^{L*}}$.

Another general property, for a uniaxial mesophase with $D_{\infty h}$ symmetry, is that only even L can appear in equation (1.2). To simplify further one has to investigate the symmetry of the molecules forming the mesophase. We shall discuss this in some detail in Chapter 3. By now we consider the simplest case of all, which arises of course when the molecules are cylindrically symmetric. Then a rotation about their symmetry axis should not modify the distribution function, which implies $n=0$ in equation (1.3). In other words in this limit the distribution function will depend only on the angle β between the director and the molecular symmetry axis:

$$f(\beta) = \sum_L C_L D_{0,0}^L(\beta) = \sum_L C_L P_L(\cos\beta), \quad (L \text{ even}) \quad (1.4)$$

where $C_L = (2L+1) \bar{P}_L/2$, and the $P_L(x)$ are the Legendre polynomials.

If we let $x = \cos\beta$ then

$$f(x) = \frac{1}{2} + \frac{5}{2} \bar{P}_2 P_2(x) + \frac{9}{2} \bar{P}_4 P_4(x) + \dots \quad (1.5)$$

and
$$\int_{-1}^1 f(x) dx = 1.$$

For the most common case of cylindrically symmetric molecules the order parameters are just the averages $\bar{P}_2, \bar{P}_4$ etc. and it is clear that a knowledge of all the $\bar{P}_L$ completely defines the singlet distribution; while knowing $f(x)$ all the order parameters can be calculated.

An alternative way of characterising the singlet distribution is through its moments μ_n :

$$\mu_n = \overline{x^n} = \int_{-1}^1 x^n f(x) dx. \quad (1.6)$$

These are sometimes easier to calculate as we shall see in Chapter 2, where we give a compact expression for the moments of the distribution $f(x) \propto \exp(\xi x^2)$, which is frequently used in studies of liquid crystals. The representation of the distribution function in terms of order parameters is clearly equivalent to that in terms of moments, since

$$P_L(x) = \sum_{r=0}^{[L/2]} a_{L,r} x^{L-2r}, \quad (1.7)$$

where $[n]$ means the largest integer contained in n . (Since L is even in our case $[L/2] = L/2$). The coefficients $a_{L,r}$ are defined as (37)

$$a_{L,r} = (-)^r \binom{L}{r} \binom{2L-2r}{L} / 2^L.$$

The first few example are

$$\begin{array}{ll}
 P_0 = 1 & x^0 = P_0 \\
 P_1 = x & x^1 = P_1 \\
 P_2 = (3x^2 - 1)/2 & x^2 = (P_0 + 2P_2)/3 \\
 P_3 = (5x^3 - 3x)/2 & x^3 = (3P_1 + 2P_3)/5 \\
 P_4 = (35x^4 - 30x^2 + 3)/8 & x^4 = (7P_0 + 20P_2 + 8P_4)/35 \\
 \dots\dots\dots & \dots\dots\dots
 \end{array} \tag{1.8}$$

Averaging eq.(1.7) or eqs.(1.8) gives the desired relation between moments and order parameters.

We have defined before the order parameters as averages of Wigner rotation matrices. It is worth mentioning that often in the literature an equivalent formulation in terms of cartesian, as opposed to spherical, coordinates and tensors has been used to introduce parameters that measure partial alignment. As an example, considering the case of second rank order parameters, an ordering matrix S is obtained (32). The matrix S is symmetric and traceless so that in its proper frame it can be described by just two parameters: S_{zz} and $(S_{xx} - S_{yy})$. The explicit relation between the elements of the ordering matrix and the set of $\overline{D_{m,n}^2}$ is

$$\begin{aligned}
 S_{zz} &= \overline{D_{0,0}^2} \\
 S_{xx} - S_{yy} &= \sqrt{3/2} \{ \overline{D_{0,2}^2} + \overline{D_{0,-2}^2} \} \\
 S_{xz} &= -\sqrt{3/8} \{ \overline{D_{0,-1}^2} - \overline{D_{0,1}^2} \} \\
 S_{yz} &= i\sqrt{3/8} \{ \overline{D_{0,1}^2} + \overline{D_{0,-1}^2} \} \\
 S_{xy} &= i\sqrt{3/8} \{ \overline{D_{0,2}^2} - \overline{D_{0,-2}^2} \}
 \end{aligned} \tag{1.9}$$

1.3 Determination of the Order Parameters

Let us suppose we want to measure a molecular 2nd rank tensorial property F during a time sufficiently long to allow the observation of statistically averaged quantities. If $F^{(L,m)}$ are the irreducible spherical components of F , as defined in Appendix 1, and if F is symmetric, then its only non zero components will be those of rank $L=0$ and $L=2$. If the molecule is rigid and if we neglect local field problems, the $L=0$ component, being a pure scalar, will be unchanged going from an isotropic to an oriented fluid, and we shall not consider it. We then note that F is measured in a laboratory (unprimed) frame and that the $L=2$ components of F can be written in terms of the molecule fixed components $F^{(2,m)'} as:$

$$F^{(2,n)} = \sum_m D_{n,m}^{2*}(\alpha\beta\gamma) F^{(2,m)'} \quad (1.10)$$

Taking an ensemble average we have, for a uniaxial mesophase,

$$\begin{aligned} F^{(2,n)} &= \sum_m \overline{D_{0,m}^2} F^{(2,m)'} \delta_{n,0} \\ &= \tilde{F}^{(2,0)} \delta_{n,0}, \end{aligned} \quad (1.11)$$

where we have implicitly taken the z axis of our laboratory system parallel to the director.

If the order parameters are different from zero, as in the nematic mesophase, it then turns out that the molecular anisotropy of F is not completely averaged out by the molecular motion as in an

isotropic liquid. To stress this point the tensor $\tilde{F}$ as given by equation (1.11) is often called a partially averaged tensor (38).

To illustrate the argument let us imagine the following gedankenexperiment (39): we have a rodlike molecule with only two protons interacting via a certain dipolar tensor, this being our tensor F . The proton magnetic resonance spectrum of this (imaginary) molecule in an isotropic, low viscosity, liquid would contain just one line, but on passing to the nematic state two lines, separated by an amount proportional to the partially averaged dipolar coupling tensor, will appear. The splitting increases as we lower the temperature, corresponding to the rather obvious fact that in doing so the orientational order of the system increases.

Note also that the partially averaged tensor $\tilde{F}$ has to reflect the symmetry of the mesophase. If this is uniaxial, as for nematics and smectics A, $\tilde{F}$ has to be cylindrically symmetric, as shown by equation (1.11), irrespective of the symmetry of F' . The component $\tilde{F}^{(2,0)} = \sqrt{2/3} (\tilde{F}_{||} - \tilde{F}_{\perp})$ that we measure is a linear combination of the molecular components of F and of three order parameters:

$$\tilde{F}^{(2,0)} = \overline{D_{0,0}^2} F^{(2,0)'} + 2\text{Re} \{ \overline{D_{0,1}^2} F^{(2,1)'} \} + 2\text{Re} \{ \overline{D_{0,2}^2} F^{(2,2)'} \} . \quad (1.12)$$

Because of the structure of equation (1.12) it is clear that some simplification can be achieved when we work either in the principal coordinate system of the ordering tensor, i.e. the one in which $\overline{D_{0,\pm 1}^2} = 0$, or in the principal system of F' , where $F^{(2,\pm 1)'} = 0$ and $F^{(2,2)'}$ equals $F^{(2,-2)'}$ and is real. It is usual to make one of these two assumptions,

guessing a principal system from the molecular structure if the molecule does not have sufficient symmetry elements to determine its location a priori. In this case we find:

$$\tilde{F}^{(2,0)} = \overline{D_{0,0}^2} F^{(2,0)'} + F^{(2,2)'} (\overline{D_{0,2}^2} + \overline{D_{0,-2}^2}) \quad (1.13)$$

$$= \overline{d_{0,0}^2} F^{(2,0)'} + 2F^{(2,2)'} \overline{d_{0,2}^2} \cos 2\gamma, \quad (1.14)$$

where $\overline{D_{0,0}^2} \equiv \overline{d_{0,0}^2} \equiv P_2$, and the fact that

$$D_{m,n}^L(\alpha\beta\gamma) = d_{m,n}^L(\beta) \exp(-im\alpha - in\gamma)$$

(c.f. Appendix 1) has been used. In particular, if F' has cylindrical symmetry, $F^{(2,2)'} = 0$ and we obtain

$$\tilde{F}^{(2,0)} = \overline{P}_2 F^{(2,0)'}, \quad (1.15)$$

which gives immediately

$$\overline{P}_2 = (\tilde{F}_{11} - \tilde{F}_{11}') / (F_{11}' - F_{11}') = \Delta\tilde{F} / \Delta F'. \quad (1.16)$$

We find the same result if the molecule is cylindrically symmetric, in the sense that $\overline{D_{0,2}^2} = 0$. In these two cases the order parameter is then obtained as a ratio of the anisotropy in the partially averaged quantity $\tilde{F}$ to the molecular one. It is worth noting here that the order $\overline{P}_2$ as given by equation (1.16) is a measure of the alignment of the z axis of the molecular system we have chosen to work in. As we mentioned before one has usually two practical choices: the principal system of the molecular tensor F or the principal system of the

ordering tensor, this last one having the molecular long axis parallel to z. Since we are usually interested in the order of the long axis, it is useful to go back to equation (1.10) and suppose that the molecular primed system is always the long-axis system. We then effect one more rotation, of $(\alpha'\beta'\gamma')$, from this primed system to the principal system of the tensor F (double primed system) and then take the ensemble average.

$$\tilde{F}^{(2,0)} = \sum_{m,p} \overline{D_{0,m}^{2*}} D_{m,p}^2 (\alpha'\beta'\gamma') F^{(2,p)''}. \quad (1.17)$$

If F'' has cylindrical symmetry $F^{(2,p)''} = F^{(2,0)} \delta_{p0}$. If the ordering tensor is cylindrically symmetric as well then

$$\overline{D_{0m}^2} = \overline{D_{00}^2} \delta_{0m}$$

and we find

$$\tilde{\Delta F} / \Delta F'' = \tilde{F}^{(2,0)} / F^{(2,0)''} = \overline{D_{0,0}^2} D_{0,0}^2 (\beta'). \quad (1.18)$$

Even with these assumptions of cylindrical symmetry we see that we need to know the angle β' between the long axis and the principal axis of F to be able to determine meaningful values of $\overline{D_{0,0}^2} = \overline{P_2}$.

An extreme example is the case that the two axis are perpendicular i.e. $\beta' = \pi/2$. Then $\tilde{\Delta F} / \Delta F'' = -\overline{P_2}/2$ and the measured apparent order parameter i.e. the quantity on the left hand side is negative and goes from -1/2 to 0. This case is often encountered in electron resonance studies for disclike molecules like vanadyl acetylacetonate (40,41).

Another limiting case is that the two axis are at the "magic" angle (i.e. $\cos\beta' = 1/\sqrt{3}$) so that $D_{0,0}^2(\beta') = 0$ and no measurable effect ΔF is emerging. As an example if F is a C^{13} chemical shift tensor the corresponding lines will be unshifted changing the temperature and even going to the isotropic phase (42). Of course if the principal system of F is along the long axis we recover the familiar expression $\Delta F/\Delta F'' = \overline{P}_2$.

A more complicated case arises when the ordering tensor is not cylindrically symmetric (43). We then have two independent order parameters to determine: $\overline{D_{0,0}^2}$ and $\text{Re} \{ \overline{D_{0,2}^2} \}$ and at least two independent measures are obviously needed.

Additional complications can arise if the molecules considered are not rigid (44,45). More assumptions are then required to keep the problem manageable, such as assuming that the internal motions are decoupled from the reorientation of the molecule as a whole and that they are so fast on the experimental time scale that only their average effect need be considered. We shall not treat this problem in more detail since in this thesis we deal mainly with rigid molecules and we shall instead return, for the sake of clarity, to the simplest case of a rigid cylindrically symmetric molecule with a cylindrically symmetric tensor F .

If we consider again equation (1.16) we have that the quantity $\Delta F'$ is a molecular constant, relatively independent of temperature and other state variables, so that it should only scale $\overline{P}_2$: if we plot $\Delta F'$ against temperature we will have the same shape of the plot of $\overline{P}_2$ vs. T . However, if the absolute magnitude of the order parameter has to be determined, the problem is how to find the value of the molecular

quantity F' in the nematic phase because, even if the free molecule one is known, local field effects can alter it in an unpredictable manner. Up to now we have in fact been talking of a single molecule quantity F , while it is clear that what we measure is a macroscopic quantity corresponding to it and containing contributions from all molecules in the sample. Our discussion is thus fitting to the case in which the intermolecular couplings have a negligible effect on the quantity F as, for example, can happen in practice for the magnetic susceptibility χ , (1). In this case the macroscopic tensor is simply

$$\chi^{(2,m)} = \rho F \chi^{(2,m)} .$$

where ρ is the number density.

In other cases it is clearly possible to measure a macroscopic quantity (dielectric constant, refractive index tensor etc...) but the relation of this to the corresponding molecular property is much more complicated and usually unknown. What is often done is to invoke some model for the local field or some empirical expressions. See as an example the use of Vuks (46) and Neugebauer (47) equations by Chandrasekhar and his group when F is the electric polarizability (48). The experimental method mainly discussed in this thesis will be electron spin resonance spectroscopy (38). We shall deal with very dilute ($\sim 10^{-4}M$) solutions of stable free radicals (spin probes). In our case then we can safely rule out intermolecular or local field problems but we have of course an additional complication in that we are measuring properties (ordering parameters and correlation times) of a solute molecule and not of the liquid crystal itself. We shall return to this

problem in Chapter 4.

It is maybe worth while to point out here that most of the techniques measure only the order parameter $\overline{P}_2$. Apart from NMR experiments involving solute molecules with the aim of determining their structure (43,44), the assumption of cylindrical symmetry is usually made and equation (1.18) is used. In this case the apparent order parameter measured is in error of an amount $\sim |F^{(2,2)'} D_{0,2}^2 / F^{(2,0)'}|$. We shall study the effect of deviations from cylindrical symmetry in more detail in Chapter 3.

Even if the molecule is cylindrically symmetric it would be of some importance to determine the higher rank order parameters $\overline{P}_4, \overline{P}_6$ etc. However, as directly measurable quantities of rank higher than two are rather difficult to find, one has to turn to indirect methods. As an example a technique able to measure the mean square value of a 2nd rank molecular quantity will yield values of $\overline{P}_4$. It is in fact easy to prove that

$$\begin{aligned} (\tilde{F}^{(2,0)} / F^{(2,0)'})^2 &= (\tilde{F}_{\parallel} - \tilde{F}_{\perp})^2 / (F'_{\parallel} - F'_{\perp})^2 = \\ &= \frac{1}{5} + \frac{2}{7} \overline{P}_2 + \frac{18}{35} \overline{P}_4. \end{aligned} \quad (1.19)$$

There are at present only two techniques used to measure $\overline{P}_4$. One is Raman scattering, used by Priestley and Pershan (50,51). The molecular quantity F' is in this case the differential polarizability tensor for a certain localized Raman active mode. For example a probe like N-(p'-butoxybenzylidene)-p-cyanoaniline is dissolved in a nematic and the strong line coming from the $C \equiv N$ stretching mode is studied.

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The other technique consists in analyzing the electron resonance linewidth of a radical dissolved in a liquid crystal and has been developed by our group (52-55). It is worth pointing out that both techniques have been used to study solutes and not the liquid crystal directly and also that both of them rely on certain assumptions. In particular the first one is complicated by local field and multiple scattering problems (1).

We shall discuss in detail the second technique in this thesis; for the moment we note that $\overline{P}_4$ measurements on exactly comparable systems, which would allow a cross check of the two different techniques, do not exist as yet. This comparison would be particularly interesting in view of some surprising results obtained by using the Raman scattering method. For instance negative values of P_4 have been obtained (50,51), in contrast with the predictions of the current theories of the nematic phase (c.f. Chapter 2).

CHAPTER TWO

A STATISTICAL THEORY OF THE NEMATIC PHASE

2.1 Introduction

The task of developing a molecular theory for phases of anisotropic particles seems at first sight a formidable one. To quote de Gennes (1): "The statistical mechanics of liquids is difficult; the statistical mechanics of nematics is still worse". While this is certainly true in general, fortunately we can take liquid crystals also as an illustration of the so-called inventor's paradox (56) i.e. that sometimes a more complicated problem is easier to solve than a simple one.

To be more specific, we have to define what we mean by a molecular theory of liquid crystals. Let us first state that we are not really aiming at a theory capable of predicting, for example, all the various phase transitions and in particular the solid-nematic or the liquid-gas transition for an assembly of anisotropic particles. As is well known these problems are practically untractable even for systems composed of much simpler molecules. What we are seeking instead is a theory able of describing the most characteristic properties of liquid crystals. That is, first of all, that they undergo an orientational transition from a disordered, isotropic phase, i.e. an ordinary liquid, to a phase where an orientational order parameter such as $\overline{P}_2$ is different from zero. Apart from this qualitative prediction of the existence of such a phase transition, a theory of the nematic mesophase is expected to predict, or at least reproduce

the behaviour and the values of the relevant thermodynamical quantities at this transition. In particular the following experimental observations should be explained by the theory: the isotropic-nematic (I-N) transitions are of first order type with latent heats typically of 1 KJ mol^{-1} (32), small volume changes i.e. $\sim 0.3\%$ (57), small entropy changes i.e. $S^{(K)}/R \sim 0.3$ (6). The value of the order parameter $\bar{P}_2$ at the I-N transition is usually found to be about 0.4, (32). Finally values of the higher rank order parameters such as $\bar{P}_4$, though difficult to obtain experimentally (c.f. Chapter 1), are very valuable in verifying theoretical predictions.

Having said what we expect of a theory of liquid crystals, we shall proceed to make a brief survey of the existing theories. These have a relatively long history dating back e.g. to Born in 1916 (58) and Zwetkoff in 1942 (31), although the first really successful attempt at developing a theory was made by Maier and Saupe (M-S) in 1960 (57). To have a liquid crystal it is quite clear that a necessary condition is a strongly anisotropic intermolecular potential. Maier and Saupe based their approach on the assumption that the anisotropic potential between two molecules, considered rigid and cylindrically symmetric, comes solely from London dispersion forces. This attractive interaction is then treated in the molecular field approximation, generalizing the well known Weiss model of ferromagnetism (59). The spirit of the molecular field treatment is to replace the detailed interaction between molecules (spins in the case of magnetism) by an effective potential or pseudopotential representing the average interaction of all other molecules with the one in question.

The M-S anisotropic pseudopotential obtained in this way has the form

$$U(x) = (A \bar{P}_2 / V^2) P_2(x), \quad (2.1)$$

where x is the cosine of the angle between the symmetry axis of the molecule and that of the mesophase, A is a molecular constant, proportional to the square of $(\alpha_{||} - \alpha_{\perp})$, the anisotropy in the polarizability tensor of the molecules and V is the volume of the system. The remaining quantity, $\bar{P}_2$, is just the normal order parameter defined in Chapter 1. It is determined from the consistency condition as

$$\bar{P}_2 = \int P_2(x) \exp\{-\beta U(x)\} dx / \int \exp\{-\beta U(x)\} dx, \quad (2.2)$$

where $\beta \equiv -1/kT$.

It is easy to see that $\bar{P}_2=0$ is always a solution of equation (2.2), corresponding to a disordered system. As we shall discuss later (for a mathematically equivalent model) there is another solution with $\bar{P}_2 \neq 0$, corresponding to the nematic mesophase, which exists below a certain critical temperature T_K . The value of $\bar{P}_2$ at the transition is predicted to be 0.43 (57) in reasonably good agreement with experiment. Another prediction of the M-S theory is that $\bar{P}_2$ should be a universal function of the reduced temperature $T^* = T/T_K$, where T_K is the absolute nematic isotropic transition temperature. In figure 2.1 we compare a plot of $\bar{P}_2$ vs. T^* according to M-S theory with some typical experimental results. We see that the agreement between theory and experiment is generally good but also that there is not really a universal curve. Another prediction is that the entropy at the

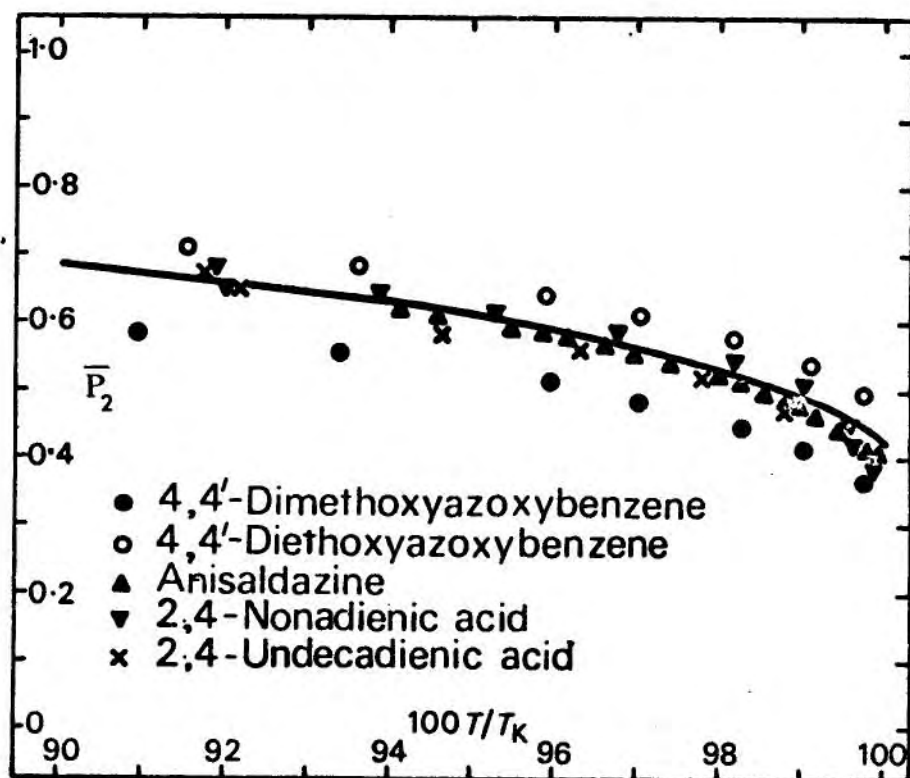


Figure 2.1 The orientational order $\bar{P}_2$ plotted as a function of the reduced temperature for a number of nematogens (2). The continuous line is the prediction of the Maier-Saupe theory.

transition $S^{(K)}/R$ should be 0.42. Again this is in qualitative agreement with experiment.

Although very successful and widely used, the M-S theory has been subject to some criticism. For instance, M-S theory does not appear to consider steric or indeed any type of intermolecular forces except dispersion. Kaplan and Drauglis (60) have noticed that an order of magnitude calculation based just on dispersion forces gives a far too low value for the interaction parameter A as compared to the value determined from the transition temperature T_K . Their calculation is itself open to criticism since the actual values of the molecular polarizability anisotropy cannot be extracted from the refractive index data with any certainty because of local field complications. None the less there is some doubt the polarizability alone is responsible for the existence of liquid crystals. Other discrepancies, between the Maier-Saupe theory and experiment this time, come from the fact that the volume dependence of the transition temperature, as measured by the value of $(\partial \ln T / \partial \ln V)_{\bar{P}_2}$ is nearer to four (61) than to the value of two predicted from equation (2.1).

Apart from dispersion forces the other obvious candidate as an orienting factor and as responsible for liquid crystal formation is a steric (repulsive) one in combination with the anisotropy in the molecular shape i.e. with the fact that nematogen molecules are rather elongated and similar to rigid rods. Many authors, starting from Onsager in 1942 (62) have shown that systems of elongated objects interacting with just a hard potential i.e.

$$U_{12} = \begin{cases} \infty & \text{if there is overlap} \\ 0 & \text{if there is no overlap} \end{cases} \quad (2.3)$$

can give a transition to an oriented phase when the density of elongated objects becomes sufficiently high. The steric theories (62,63), however, have not been extremely successful. Firstly it is clear that purely steric models give a phase transition independent of temperature and so they are rather inappropriate for the treatment of thermotropic liquid crystals. Apart from this difficulty, they predict values of the order parameter at the transition far too high (~ 0.8) and also the entropy change is predicted to be much larger than observed. A Monte Carlo calculation (64) has been performed on a system of hard spherocylinders (65) but failed to exhibit an orientational phase transition even after over 50×10^6 configurations had been generated.

While then it seems clear that steric forces as well as dispersion are relevant to describe interactions between nematogen molecules it is likely that a blend of the two and possibly of other factors such as deviations from cylindrical symmetry, flexibility, effects of electrostatic multipoles will have to be taken into account before we have a proper understanding of the relation between the nematic behaviour of a molecule and its structure. In view of all these complications it may now become difficult to see why the Maier-Saupe theory is so successful. The reason is probably a very simple one, namely that the M-S potential has the correct functional form. A simple heuristic argument to illustrate this point is that the potential for a rod in a (molecular) field of uniaxial symmetry will be a function of the angle β between rod and field symmetry axis only. This means

that we can expand $U(x)$, where $x = \cos \beta$, as a sum of Legendre polynomials and if we approximate this series with the first symmetry allowed term then $U(x) \sim c P_2(x)$. We do not know anything about the coefficient c but on the other hand, since $U(x)$ has to vanish in the isotropic phase, it is obvious that the simplest correct assumption is that c will be proportional to the order parameter i.e.

$$U(x) = c' \bar{P}_2 P_2(x), \quad (2.4)$$

which is essentially the Maier - Saupe result but where now c' is essentially an adjustable parameter.

A general mean field approach has been developed by Humphries, James and Luckhurst (H-J-L) (33). Their treatment consists of writing down the intermolecular potential between two molecules as a Pople expansion i.e. expanding the potential in a complete product basis set of spherical harmonics of the orientations of the two molecules (66,67). Three successive averages are then taken to obtain the pseudopotential for a single molecule. The first is over all the possible orientations of the intermolecular vector in space, the second over all the orientations of the second molecule in the molecular field and the third average over the intermolecular distances. Their result is

$$U(x) = \sum_L u_L \bar{P}_L P_L(x), \quad (L \text{ even}) \quad (2.5)$$

where $\bar{P}_L$ are the orientational order parameters determined self-consistently by a set of equations similar to equation (2.2);

u_L is an average interaction coefficient, which is a function of molecular properties as well as of the volume of the system. Humphries, James and Luckhurst studied in particular the effect of retaining terms up to $L=4$ on the properties of the mesophase. They found that in many cases the quartic term is necessary to reproduce quantitatively the temperature dependence of $\overline{P}_2$ and in particular its value at the transition (68). In the H-J-L theory the volume dependence of u_L is assumed to be $u_L = u_L^0 V^{-\gamma}$. A fitting of the temperature dependence of $\overline{P}_2$ gives a value of $\gamma=4$ (69), in excellent agreement with the independent measurement of $(\partial \ln T / \partial \ln V)_{\overline{P}_2}$ by Mc Coll and Shih (61).

Both in M-S and H-J-L theory the calculation starts from the pairwise intermolecular potential which is then averaged in a certain way to obtain the molecular field. While this seems a physically plausible procedure, it is, in a sense, a somewhat unconventional statistical calculation and a formal justification should be provided. It is clear in fact that in general one has just a total potential energy for the system and that the various averages have to come from a proper partition of this total potential. It would be more satisfactory to start from the partition function for a system of anisotropic particles and proceed by successive, well-defined approximations to obtain an effective orientational distribution and partition function. In Section 2.2 we provide this more rigorous treatment.

2.2 A Molecular Theory of the Nematic Mesophase

The configurational partition function for a system of N interacting rigid particles with positions defined by a vector R and orientation described by a set of three Euler angles $(\alpha, \beta, \gamma) \equiv \Omega$ can be written as (70)

$$Q_N = (1/N!) \int \{dR\} \{d\Omega\} \exp\{-\beta U(R_1 \dots R_N, \Omega_1 \dots \Omega_N)\}. \quad (2.6)$$

The notation $\{dR\}$ and $\{d\Omega\}$ is an abbreviation for the volume elements in configurational space i.e. $\{dR\} = d^3R_1 \dots d^3R_N$ and $\{d\Omega\} = d\Omega_1 \dots d\Omega_N$. As usual, $\beta = 1/(kT)$ where k is the Boltzmann constant and T the temperature. The potential energy $U(R_1 \dots R_N, \Omega_1 \dots \Omega_N)$ of the system is a function of both the positions and the orientations of all the molecules. In general these will be coupled in a complicated way and the problem will be practically insoluble but, on the other side, we expect that liquid crystals can be described effectively in terms of an orientational potential only. In this section we start from equation (2.6) and derive an effective orientational potential and partition function. This is then compared with the mean field results of Humphries-James-Luckhurst (33) and Maier-Saupe (57), which were obtained in a more ad hoc way. One of the aims will be to define the various approximations involved to obtain these results and to indicate possible generalizations and improvements. The spirit is similar to that adopted in a paper by Schultz (71), with the difference however that he essentially poses the problem and then turns to a specific model where the molecules can only assume discrete positions and orientations. Instead we shall aim to be as general as

possible.

As a starting point let us assume that the total potential can be separated into a part U_S depending on the position of the molecules only together with an anisotropic part U_A depending on the distance between molecules as well as their orientation:

$$U = U_S + U_A. \quad (2.7)$$

This assumption allows us to rewrite the partition function as

$$\begin{aligned} Q_N &= (1/N!) \int \exp(-\beta U_S) \exp(-\beta U_A) \{dR\} \{d\Omega\} \\ &= (1/N!) \int \exp(-\beta U_S) \{dR\} \int \{d\Omega\} \frac{\exp(-\beta U_S) \exp(-\beta U_A) \{dR\}}{\exp(-\beta U_S) \{dR\}} \\ &= Q_N^S \cdot \int \{d\Omega\} \overline{\exp(-\beta U_A)}, \end{aligned} \quad (2.8)$$

where Q_N^S is the partition function relating to the position of the molecules (their centres of mass say):

$$Q_N^S \equiv (1/N!) \int dR_1 dR_2 \dots dR_N \exp\{-\beta U_S(R_1 \dots R_N)\}, \quad (2.9)$$

and the upper bar in equation (2.8) indicates a positional average. We see then that even after separation of the potential in two parts we are not yet able to factorize the total partition function into positional and anisotropic contributions as we should like. To achieve this Schultz (71) proves that

$$Q_N \geq Q_N^A Q_N^S, \quad (2.10)$$

where

$$Q_N^A \equiv \int d\Omega_1 \dots d\Omega_N \exp(-\beta U_A), \quad (2.11)$$

is an orientational partition function, and then simply takes (2.10) as an equality. This has the obvious disadvantage of not indicating how to improve the approximation. Instead we shall then develop $\overline{\exp(-\beta U_A)}$ in cumulants as follows:

$$\overline{\exp(-\beta U_A)} = \exp\{\langle \exp(-\beta U_A) - 1 \rangle_C\}, \quad (2.12)$$

where $\langle \dots \rangle_C$ denotes a cumulant average (72). The first few terms in this expansion are:

$$\begin{aligned} \overline{\exp(-\beta U_A)} &= \exp\{-\beta \bar{U}_A + \frac{\beta^2}{2} (\bar{U}_A^2 - \bar{U}_A^2) \\ &\quad - \frac{\beta^3}{6} (\bar{U}_A^3 - 3\bar{U}_A^2 \bar{U}_A + 2\bar{U}_A^3) + \dots\} \\ &= \exp(-\beta \bar{U}_A) \cdot \exp(\text{correction terms}) \end{aligned} \quad (2.13)$$

We see then from equations (2.8) and (2.13) that the inequality (2.10) is indeed verified, being the quantity (correction terms) a non negative function.

We would now like to retain, for the sake of simplicity, only the first non-zero cumulant, i.e. $\bar{U}_A$, which amounts essentially to a

high temperature approximation. This does not seem reasonable at first sight, since $\bar{U}_A$ is an energy referred to the whole system and so is proportional to the number of particles N . On the other hand it is clear that the validity of the expansion i.e. the structure of the equations that we get should be independent of the number of molecules in the system. The solution to this apparent paradox often appearing in this sort of calculation is simply that the second term in the series $(\bar{U}_A^2 - \bar{U}_A^2)$, is still proportional to N and not to N^2 because of the finite range of the intermolecular potential (73). It then turns out the condition of applicability of the expansion is that $\bar{U}_A/N$, i.e. the single particle energy, is small compared to kT . For the moment we shall then retain only the first term in equation (2.13) (but others terms can be treated in the same way) and try to give $\bar{U}_A$ in more detail. Let us first introduce a pairwise additivity assumption:

$$U_A = \sum_{i < j} U(i, j), \quad (2.14)$$

which allows $\bar{U}_A$ to be written as:

$$\bar{U}_A = \sum_{i < j} \int d^3R_i d^3R_j U(i, j) \frac{\prod_{k \neq i, j} d^3R_k \exp\{-\beta U_S(R_1 \dots R_N)\}}{\int d^3R_1 \dots d^3R_N \exp\{-\beta U_S(R_1 \dots R_N)\}} \quad (2.15)$$

$$= \sum_{i < j} \int d^3R_i d^3R_j U(i, j) f(i, j) \quad (2.16)$$

The pair distribution $f(i, j)$ gives the probability of finding the centres of mass of molecules i and j respectively at R_i and R_j .

Since we have assumed U_S to be isotropic, $f(i,j)$ will depend only on $|R_i - R_j| = R_{ij}$ and we could write $f(i,j) = g(R_{ij})/V^2$, where V is the volume of the system and $g(R)$ the pair distribution function of the centres of mass. For large separations $f(i,j)$ goes as $1/V^2$. Notice that the isotropy in $f(i,j)$ comes directly from equation (2.7) without further assumptions or, viceversa, that within that approximation it is not possible to allow for deviations from spherical symmetry of $g(R)$ even though such anisotropy exists in liquid crystals.

Since the explicit forms of $U(i,j)$ and $f(i,j)$ in equation (2.16) are not known, to proceed further we shall try to extract as much information as possible from their general properties. We can write the anisotropic intermolecular potential $U(i,j)$ in a (complete) product basis set of Wigner rotation matrices (39) in the orientations of the two molecules i.e. as a series of terms of increasing tensorial rank (66,67). Choosing a coordinate system, which we call the intermolecular or IM system, with the z axis along the $R_{ij} \equiv R_i - R_j$ vector, this has the form

$$U(i,j) = \sum'_{L_1 L_2 m_1 m_2} (R_{ij}) D_{m,n_1}^{L_1} (\Omega_{i-R_{ij}}) D_{-m,n_2}^{L_2} (\Omega_{j-R_{ij}}), \quad (2,17)$$

where Ω_{i-R} defines the orientation of molecule i in this system and the prime on the summation indicates that the $L_1 = 0, L_2 = 0$ term is excluded, since it constitutes part of the scalar potential.

To avoid the inconvenience of every pair of molecules defining a different coordinate system we now rewrite equation (2,17) in a laboratory system using the relation (see Appendix 1)

$$D_{m,n}^L (\Omega_{i-R_{ij}}) = \sum_q D_{q,m}^{L*} (\Omega_{R_{ij}-L}) D_{q,n}^L (\Omega_{i-L}), \quad (2,18)$$

where $\Omega_{R_{ij}-L}$ and Ω_{i-L} represent a rotation from a laboratory system to the IM system and to a coordinate system fixed on molecule i respectively. This gives:

$$U(i,j) = \sum' u_{L_1 L_2 m_1 n_2}(R_{ij}) D_{q_1, n_1}^{L_1}(\Omega_{i-L}) D_{q_2, n_2}^{L_2}(\Omega_{j-L}) \quad (2.19)$$

$$\times D_{q_1, m}^{L_1 *}(\Omega_{R_{ij}-L}) D_{q_2, -m}^{L_2 *}(\Omega_{R_{ij}-L}).$$

Substituting in equation (2.16) we obtain

$$\bar{U}_A = V \sum_{i < j} \sum_{L_1, L_2, n_1, n_2} \int u_{L_1 L_2 m_1 n_2}(R_{ij}) f(R_{ij}) R_{ij}^2 dR_{ij} \quad (2.20)$$

$$\times \left\{ D_{q_1, m}^{L_1 *} D_{q_2, -m}^{L_2 *} d\Omega_{R_{ij}-L} \right\}$$

$$\times D_{q_1, n_1}^{L_1}(\Omega_{i-L}) D_{q_2, n_2}^{L_2}(\Omega_{j-L}).$$

Since $f(R_{ij})$ is isotropic, the integral over the two Wigner rotation matrices gives immediately

$$(-)^{q+m} \frac{4\pi}{(2L+1)} \delta_{q_1, -q_2} \delta_{m, m} \delta_{L_1, L_2}, \quad (2.2)$$

and we can rewrite the positionally averaged anisotropic potential as

$$\bar{U}_A = \sum_{i < j} \sum'_{L, n_1 n_2} c_{Ln_1 n_2} \sum_q (-)^q D_{q, n_1}^L(i) D_{-q, n_2}^L(j). \quad (2.22)$$

Here we have defined

$$c_{Ln_1 n_2} = \frac{4 \pi V}{2L+1} \sum_m (-)^m \int u_{LLmm_1 n_2}(R) f(R) R^2 dR, \quad (2.23)$$

and written (Ω_{i-L}) as (i) , since from now on all the orientations are measured from the laboratory frame and no confusion should arise.

From equation (2.22) we see that $\bar{U}_A$ is a purely orientational potential: each molecule can interact, through its orientation, with any other molecule, with an average "strength of interaction" coefficient $c_{Ln_1 n_2}$ coming from the smear over all the molecules of the local interactions. Thus, even very short range interactions give rise to an orientational potential not dependent on distance i.e. of infinite range, while of course the coefficients $c_{Ln_1 n_2}$ are infinitesimal in magnitude. For instance, if we suppose the molecule can interact with only z neighbours and with an average potential ϵ , the coefficients $c_{Ln_1 n_2}$ will be of order $z\epsilon/2N$.

Substitution of the expression for $\bar{U}_A$ in equation (2.11) shows that the problem of the evaluation of the orientational partition function has been reduced to calculating

$$Q_N^A = \int d\Omega_1 d\Omega_2 \dots d\Omega_N \exp\{-\beta \sum_{i < j} U(\Omega_i, \Omega_j)\}, \quad (2.24)$$

where

$$U(\Omega_i, \Omega_j) = \sum'_{L, q, n_1, n_2} (-)^q c_{Ln_1 n_2} D_{q, n_1}^L(i) D_{-q, n_2}^L(j). \quad (2.25)$$

The similarity between this potential and that used to treat orientational and magnetic transitions on lattices is quite striking (74-76). However, a difference with the lattice treatments that is worth pointing out is that they usually restrict the orientational (or spin) interactions to nearest neighbours only, i.e. they have a local interaction, while here, since we have averaged over the distances, only infinite range orientational interactions appear.

We could now go on with the potential in equation (2.22) and keep the treatment quite general but, since this complicates the book-keeping without changing the physics of the problem, we shall restrict ourselves to the case of cylindrically symmetric molecules (i.e. $n_1=n_2=0$) with second rank interactions only (i.e. $L=2$). Then the anisotropic potential will be

$$\bar{U}_A = \sum_{i<j} \sum_q (-)^q c_2 D_{q,0}^2(i) D_{-q,0}^2(j) \quad (2.26)$$

$$= c_2 \sum_q \sum_{i<j} D_{q,0}^2(i) D_{q,0}^{2*}(j) \quad (2.26')$$

$$= c_2 \sum_{i<j} P_2(\cos \Omega_{i-j}).$$

Here $c_2 \equiv c_{200}$ and the angle Ω_{i-j} in equation (2.26') is the difference of the two rotations Ω_i and Ω_j . In equation (2.26') we have rewritten the potential by using the spherical harmonics addition theorem in a form that puts in evidence that the potential is invariant under rotation of the laboratory system and of the long axis of the molecules. We now write the Wigner rotation matrices in equation (2.26) as

$$D_{q,0}^2(i) = D - \omega_q(i), \quad (2.27)$$

where $\omega_q(i)$ is a new orientational function and D a separation parameter to be determined variationally later on. We shall show that this provides a way of decoupling the potential into a "molecular field" part, in agreement with the Humphries-James-Luckhurst one (33), and into a correction term. We shall also show that the separation parameter D is, in the molecular field limit, just an orientational average of a Wigner rotation matrix i.e. an order parameter. To begin with we substitute equation (2.27) in equation (2.26) and find

$$\overline{U}_A = U_0 + U_1, \quad (2.28)$$

where

$$U_0 = c_2 \sum_q (-)^q \left\{ -\frac{N^2}{2} D^2 + \frac{N}{2} \left[D \sum_i D_{-q,0}^2(i) + D \sum_i D_{q,0}^2(i) \right] \right\}, \quad (2.29)$$

provided the number of particles is so large that $N(N-1) \sim N^2$, and

$$U_1 = c_2 \sum_q (-)^q \sum_{i < j} \omega_q(i) \omega_{-q}(j). \quad (2.30)$$

We shall take U_0 , which is linear in the orientational functions, as our zeroth order or unperturbed potential and U_1 , which is quadratic in the same quantities, as a correction. Accordingly the orientational partition function can be written as:

$$\begin{aligned}
 Q_N^A &= \int \exp\{-\beta \bar{U}_A\} \{d\Omega\} \\
 &= \int \exp\{-\beta U_0\} \{d\Omega\} \frac{\int \exp\{-\beta U_0\} \exp\{-\beta U_1\} \{d\Omega\}}{\int \exp\{-\beta U_0\} \{d\Omega\}} \\
 &= \Phi_N \overline{\exp(-\beta U_1)}.
 \end{aligned} \tag{2.31}$$

where the upper bar indicates the average over the unperturbed state and where we have defined a zeroth order N-particle partition function Φ_N as

$$\Phi_N \equiv \int \exp\{-\beta U_0\} \{d\Omega\} . \tag{2.32}$$

Let us now investigate more closely the parameter D. We first notice that to obtain an effective potential for a mesophase having cylindrical symmetry we have somehow to break the full rotational symmetry of the potential $\bar{U}_A$. A natural way of doing this is to include an external field term of the proper symmetry as $\zeta \sum_{i=1}^N P_2(\cos \beta_i)$ where β_i is the angle between the field direction, taken as the laboratory z axis, and the i-th molecule symmetry axis (75-77). Of course, since we are interested in the field-free system, we then let the coupling parameter ζ go to zero. If we assume that this limiting process does not interfere with our successive mathematical steps, we can take the limit at once i.e. in practice avoid writing down the field term, remembering however that the potential has now to conform to the broken symmetry. In our case this means to be invariant under rotation about the z axis and under reflection in a plane perpendicular to it. After symmetriza-

tion the potential U_0 becomes

$$U_0 = -c_2 \frac{N^2}{2} D^2 + c_2 N D \sum_{i=1}^N P_2(\cos \beta_i). \quad (2.33)$$

This in turn gives

$$\begin{aligned} \phi_N &= \int \exp\{-\beta U_0\} \{d\Omega\} \\ &= \exp\{\beta c_2 \frac{N^2}{2} D^2\} \{\phi\}^N, \end{aligned} \quad (2.34)$$

where $\{\phi\}^N$ is the N-th power of the single particle pseudo-partition function

$$\phi = \int \exp\{-c_2 \frac{ND}{kT} P_2(\cos \beta_i)\} d\cos \beta_i. \quad (2.35)$$

The value of D is now determined by minimizing the appropriate unperturbed thermodynamic potential which, since we suppose the volume is essentially constant, is the Helmholtz free energy A .

From the definition of A we have

$$A_0 = -kT \ln \phi_N \quad (2.36)$$

$$= -\frac{1}{2} c_2 N^2 D^2 - NkT \ln \phi. \quad (2.37)$$

A necessary condition for a minimum is that

$$\frac{\partial A_0}{\partial D} = -c_2 N^2 D + c_2 N^2 \bar{P}_2 = 0. \quad (2.38)$$

Thus, to minimize the free energy, the separation parameter D must satisfy the consistency equation

$$D = \bar{P}_2 = \int P_2(x) \exp\{-(\beta c_2 N \bar{P}_2) P_2(x)\} dx, \quad (2.39)$$

or, in other words, the best separation parameter is just the order parameter $\bar{P}_2$. To confirm that $D=\bar{P}_2$ is a true minimum the second derivative of the free energy $\left(\frac{\partial^2 A_0}{\partial D^2}\right)_{D=\bar{P}_2}$ has to be calculated and this will give the region of stability of the phase. We shall see an example in Section 2.4.

Let us now consider the correction term $\overline{\exp(-\beta U_1)}$. In lattice problems a method for successive systematic approximations to this type of integral has been developed (74,75). The physical idea is to consider progressively larger clusters of molecules in the molecular field produced by all the others. The unperturbed potential U_0 corresponds from this point of view to a cluster of just one molecule i.e. to the mean field approximation. The other terms allow for the short range effects, since the interactions within a cluster are treated in detail. Since our orientational potential is of infinite range we do not expect the correction term to be important, by analogy with, for example, ferromagnetic problems, where it has been shown by Kac (78) that the mean field solution becomes exact when the range of the interaction goes to infinity.

To check this point consider the first cumulant of U_1 i.e. approximate $\overline{\exp(-\beta U_1)}$ by $\exp(-\beta \bar{U}_1)$. If we rewrite U_1 as

$$U_1 = \frac{1}{2} c_2 \{N^2 D^2 - 2ND \sum_i P_2(i) + \sum_{i,j} \sum_q (-)^q D_{q0}^2(i) D_{-q0}^2(j)\}, \quad (2.40)$$

we see immediately that $U_1 \sim 0$ since at this level of approximation $D \sim \bar{P}_2$, as we have shown before. One should then retain at least terms up to β^2 and since we have rejected terms of this type during the course of the derivation, to be consistent we shall content ourselves in retaining only the unperturbed term U_0 as an approximation to the potential $\bar{U}_A$.

In summary, we have shown that starting from the total partition function for a system of N particles with anisotropic interactions it is possible to obtain an approximate orientational partition function Φ_N . Corresponding to this partition function we have an effective orientational potential U_0 which, in the case of cylindrically symmetric molecules with second rank interactions only is

$$U_0 = -\frac{1}{2} c_2 N^2 \bar{P}_2^2 + c_2 N \bar{P}_2 \sum_{i=1}^N P_2(\cos \beta_i), \quad (2.41)$$

where c_2 (or Nc_2) gives the average strength of the interaction, $\bar{P}_2$ is an order parameter and β_i is the angle between the symmetry axis of the molecule and that of the mesophase.

It is maybe worth pointing out here that the decomposition scheme we have adopted to reduce the total partition function is not the only possible one. As an example we could have introduced the separation parameters before the integration over the intermolecular separations. In general it is difficult to compare different decomposition schemes because they usually do not involve just a different ordering of the same operations but different sorts of approximations or physical assumptions as well. In any case, at the first level of approximation which is the one explicitly treated in this Chapter, the molecular field result is obtained anyway.

We are now in a position to compare our results with those obtained by Humphries, James and Luckhurst (H-J-L) and by Maier and Saupe. To do this, we notice first that H-J-L have not only retained terms with $L=2$, but, at least formally, all the terms with even L in the potential. We can do the same, by having separation parameters which are L dependent i.e. D_L , instead of D . The symmetry argument and the minimization of the free energy would then give $D_L = \bar{P}_L$, where L must be even if the mesophase has uniaxial symmetry. If we consider now the single particle partition function $\phi_1 = \{\phi_N\}^{1/N}$ and define $u_2 \equiv c_2 N$ we see that we have essentially recovered H-J-L results i.e. the effective potential of a molecule in the field of all the others is

$$U(x) = \sum_L u_L \bar{P}_L P_L(x). \quad (L \text{ even}) \quad (2.42)$$

Restriction to the first term, $L=2$, as we did before gives a potential formally analogous to the M-S one. Having established the equivalence of the treatments at this level of approximation, we may underline some other points. In this treatment we have obtained H-J-L as a first order approximation in a rather general expansion. In particular, our partition function is the proper one in the sense that we can obtain all the thermodynamic quantities from it by using the standard formulae (70,73). This sheds light on a sort of paradox of the usual mean field theory, where one has sometimes to use what seem ad hoc relations. In fact, since the mean field treatment concentrates on the single molecule potential $U(x)$, what is naturally evaluated is not the partition function but what we have already called the pseudopartition function

i.e. ϕ and not

$$\phi_1 = (\phi_N)^{1/N} = \exp(\beta u_2 \bar{p}_2^2/2) \phi .$$

Thus, as an example, the quantity $-kT \ln \phi$ will not be just the free energy, but a term $u_2 \bar{p}_2^2/2$ or in general $\sum_L u_L \bar{p}_L^2/2$ will have to be added as is usually done in practice. .

2.3 The Maier - Saupe Model

The simplest effective potential that gives a reasonably good description of the liquid crystalline phase has the angular dependence of a second Legendre polynomial. We have shown in the previous section how this potential can be obtained in a rather general way. The potential is formally equivalent to the one originally obtained by Maier and Saupe (57) and it could also be obtained on purely heuristic grounds (c.f. Section 2.1) or by using the Humphries, James and Luckhurst method (33). In this section we treat in some detail the problem of calculating the partition function, the moments and the order parameters for this Maier-Saupe like model. Since this has already been studied, the justification for the following Section lies in the fact that many of the results, particularly on the order parameters, will be used again in this thesis and that to obtain them we give a number of new and hopefully useful expressions.

The single particle partition function for the model is

$$\phi_1 = \exp(\beta u_2 \bar{P}_2^2 / 2) \phi, \quad (2.43)$$

$$\phi = 2 \exp(\beta u_2 \bar{P}_2 / 2) Z_0, \quad (2.44)$$

where we have defined a (reduced) pseudopartition function Z_0 as

$$Z_0 \equiv \int_0^1 \exp(\xi x^2) dx, \quad (2.45)$$

and $\xi = \frac{-3\beta}{2} u_2 \bar{P}_2 \equiv \frac{-3\beta}{2} c_2 N \bar{P}_2$ is the interaction parameter, which is positive if the pairwise potential favours parallel alignment. Even for this simple angular dependence the pseudopartition function is not an

elementary function of the interaction ξ . We can however express Z_0 in terms of known functions. Rewriting Z_0 as

$$\begin{aligned} Z_0 &= \int_0^1 \exp(\xi x^2) dx \\ &= \int_0^1 \exp(\xi t) t^{-1/2} (1-t)^{3/2-1/2-1} dt, \end{aligned} \quad (2.46)$$

we see that this is just the integral representation of the Kummer confluent hypergeometric function $M(a,b,z)$ (79,80) if we take $a=1/2$, $b=3/2$, $z=\xi$. In other words

$$Z_0 = M(1/2, 3/2, \xi). \quad (2.47)$$

As well as its compactness, this expression has the advantage of allowing us to use the large amount of results existing for these special functions, as we shall see in the following. Some of the most useful properties of the Kummer functions are listed in Appendix 2.

Since, as we said, Z_0 is not an elementary function of ξ it is difficult to have a feeling for how it behaves. To this purpose a simple approximate expression for Z_0 would be useful, and one is obtained in the following way. Notice first that a trivial power expansion of Z_0 is obtained from equation (2.45) by expanding $\exp(\xi x^2)$ and integrating term by term i.e.

$$Z_0 = \sum_{m=0} \xi^m / [(2m+1) \cdot m!] = 1 + \xi/3 + \xi^2/10 + \dots \quad (2.48)$$

is given in figure 2.2.

A compact expression for all the even moments of the orientational pseudodistribution $f(x) = \exp(\xi x^2)/Z_0$ can be obtained using the properties of the Kummer functions. By definition (see Chapter 1) the moments are

$$\overline{x^{2n}} = \frac{\int_0^1 x^{2n} \exp(\xi x^2) dx}{\int_0^1 \exp(\xi x^2) dx} \equiv \frac{Z_{2n}}{Z_0}. \quad (2.54)$$

It is easy to see that

$$Z_{2n} = \frac{d^n}{d\xi^n} Z_0 = \frac{d^n}{d\xi^n} M(1/2, 3/2, \xi), \quad (2.55)$$

or using the differentiation formula for $M(a, b, z)$,

$$Z_{2n} = M(n+1/2, n+3/2, \xi) / (2n+1). \quad (2.56)$$

Substitution in equation (2.54) gives the desired expression for the moments. An expression for all the Legendre polynomial averages can be obtained at once from equations (1.7) and (2.54).

Asymptotic expressions for high values of the interaction parameter can be obtained from the corresponding formulae for the Kummer functions reported in Appendix 2. At high order

$$Z_{2n} = \frac{e^\xi}{2\xi} \sum_{m=0}^{\xi} (-)^m (n + 1/2 - m)_m \xi^{-m}, \quad (\xi \rightarrow \infty), \quad (2.57)$$

where $(C)_n = C(C+1)\dots(C+n-1)$ and $(C)_0 = 1$.

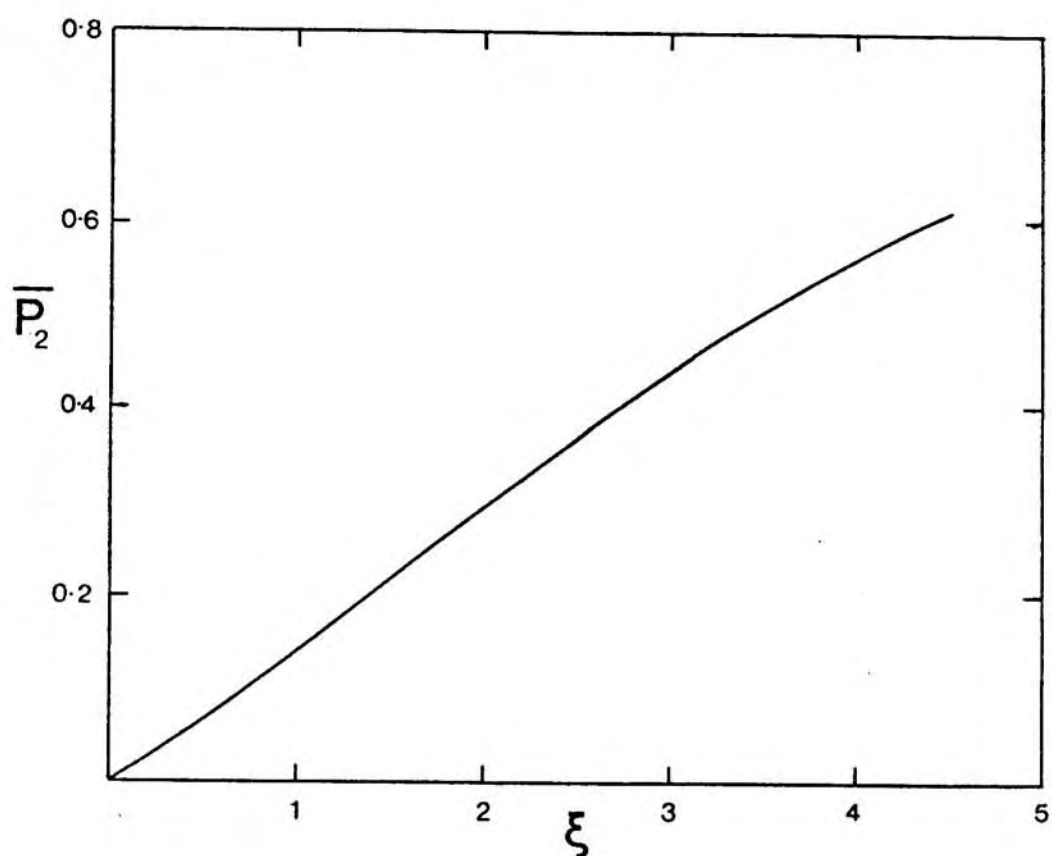


Figure 2.2 The orientational order parameter $\overline{P}_2(x)$, calculated for a pseudopotential $-\frac{U(x)}{kT} = \xi x^2$, is plotted as a function of the interaction parameter ξ .

In particular one obtains

$$\begin{aligned}\overline{x^2} &= 1 - 1/\xi - 1/(2\xi^2) + O(\xi^{-3}), \\ \overline{x^4} &= 1 - 2/\xi + 1/\xi^2 + O(\xi^{-3}).\end{aligned}\tag{2.58}$$

Or, equivalently,

$$\begin{aligned}\overline{P_2} &= 1 - 3/(2\xi) - 3/(4\xi^2) + O(\xi^{-3}), \\ \overline{P_4} &= 1 - 5/\xi + 25/(4\xi^2) + O(\xi^{-3}).\end{aligned}\tag{2.59}$$

We shall return to the very high order limit in Chapter 5, where we show that the same asymptotic results for the order parameters can be obtained also for the more general potential $U(x) = \sum C_L P_L(x)$. Even retaining just the term in ξ^{-1} the asymptotic expression works rather well, especially for $\overline{P_2}$, when $\xi > 6$. In Table 2.1 some values of $\overline{P_2}$ and $\overline{P_4}$ obtained in this way are compared with values obtained by numerical integration.

Low order expansions for the parameters $\overline{P_L}$ can be obtained easily from equation (2.48). We just give the result for $\overline{P_2}$:

$$\overline{P_2} = 2\xi/15 + 4\xi^2/315 + O(\xi^3)\tag{2.60}$$

When the limiting expressions for high and low order are not applicable one has in general to resort to numerical calculation to determine the order parameters. Since it is sometimes necessary (e.g. in linewidth studies, c.f. Chapter 5 and 6) to generate a large number of these order parameters $\overline{P_L}$ even of relatively high rank (up to $L=30$ say) the problem of their efficient

TABLE 2.1 The order parameters $\bar{P}_2$ and $\bar{P}_4$ calculated by numerical integration and from the asymptotic expansion equation(2.59) truncated at the first term

ξ	$\bar{P}_2$	$\bar{P}_2$ (asympt.)	$\bar{P}_4$	$\bar{P}_4$ (asympt.)
5	0.646	0.700	0.287	0
6	0.712	0.750	0.361	0.167
7	0.759	0.786	0.425	0.286
8	0.793	0.812	0.480	0.375
9	0.819	0.833	0.526	0.444
10	0.839	0.864	0.566	0.500
11	0.855	0.864	0.600	0.545
12	0.868	0.875	0.629	0.583
13	0.879	0.885	0.654	0.615
14	0.888	0.893	0.676	0.643
15	0.896	0.900	0.695	0.667
16	0.903	0.906	0.713	0.687
17	0.909	0.912	0.728	0.706
18	0.914	0.917	0.742	0.722
19	0.919	0.921	0.755	0.737
20	0.923	0.925	0.766	0.750
21	0.927	0.929	0.776	0.762
22	0.930	0.932	0.786	0.773
23	0.933	0.935	0.795	0.783
24	0.936	0.937	0.803	0.792
25	0.939	0.940	0.810	0.800
30	0.949	0.950	0.840	0.833
35	0.957	0.957	0.862	0.857
40	0.962	0.962	0.879	0.875

computation poses. One possibility is to generate the moments $\overline{x^L}$ in a recursive way, which is very easy to do, and then use equation (1.7) to obtain the $\overline{P_L}$ from these. However this is not so convenient from the numerical point of view since it implies the evaluation of the (small) coefficients $a_{L,r}$ in equation (1.7) which are ratios of large factorials. Moreover it is more satisfactory to have a recursion relation for order parameters without intermediaries. This prompted us to derive such a recurrence relation as we shall now describe. As it is well known (37)

$$L P_L(x) = (2L-1)x P_{L-1}(x) - (L-1) P_{L-2}(x). \quad (2.61)$$

Multiplication of both sides by the distribution function and integration gives

$$L \overline{P_L} = (2L-1)\overline{xP_{L-1}} - (L-1) \overline{P_{L-2}}.$$

The problem is then to evaluate $\overline{xP_{L'}}$, where $L' = L-1$ is odd. Integrating by parts, using the fact that $P_{L'}(0)=0$ for odd L' , and remembering the relation (37)

$$\frac{d}{dx} P_{L'}(x) = (2L'-1)P_{L'-1} + (2L'-5)P_{L'-3} + (2L'-9)P_{L'-5} + \dots + P_0, \quad (L' \text{ odd}) \quad (2.62)$$

we finally obtain

$$\overline{P_L} = \frac{(2L-1)}{2L\xi} \{ \exp(\xi)/Z_0 - \int_{n=0}^{(L-2)/2} [(2L-3-4n) + \frac{2\xi(L-1)}{(2L-1)} \delta_{0n}] \overline{P_{L-2-2n}} \}, \quad (L \text{ even}) \quad (2.63)$$

This allows recurrent computation of every $\bar{P}_L$ in terms of Z_0 . As an example we can write down the explicit expression for the first three order parameters i.e.

$$\bar{P}_2 = \frac{3}{4\xi} \left\{ \frac{\exp \xi}{Z_0} - \left(1 + \frac{2\xi}{3} \right) \right\}, \quad (2.64)$$

$$\bar{P}_4 = \frac{7}{8\xi} \left\{ \frac{\exp \xi}{Z_0} - \left(5 + \frac{6\xi}{7} \right) \bar{P}_2 - 1 \right\}, \quad (2.65)$$

$$\bar{P}_6 = \frac{11}{12\xi} \left\{ \frac{\exp \xi}{Z_0} - \left(9 + \frac{10\xi}{11} \right) \bar{P}_4 - 5\bar{P}_2 - 1 \right\}, \quad (2.66)$$

According to the Maier-Saupe model the knowledge of one order parameter permits the prediction of all the others. (e.g. by using equation (2.63). In figures 2.3, 2.4 the Maier-Saupe orientational order parameters $\bar{P}_2$ and $\bar{P}_4$ are plotted one against the other for positive and negative values of the interaction parameter ξ . It may be noticed that $\bar{P}_4$ is always predicted to be positive even when $\bar{P}_2$ is negative (e.g., for a disclike solute molecule whose symmetry axis tends to be perpendicular to the director).

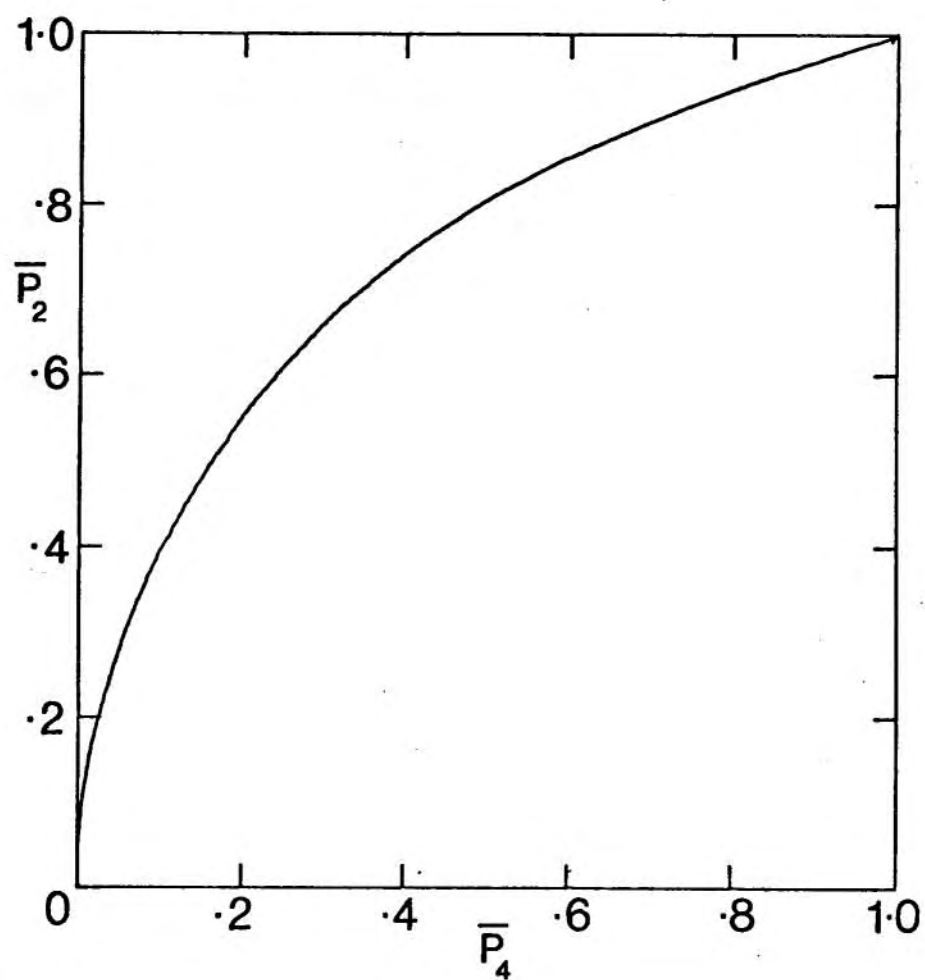


Figure 2.3 The relation between the order parameters $\overline{P}_2$ and $\overline{P}_4$ according to the Maier-Saupe model for positive $\overline{P}_2$.

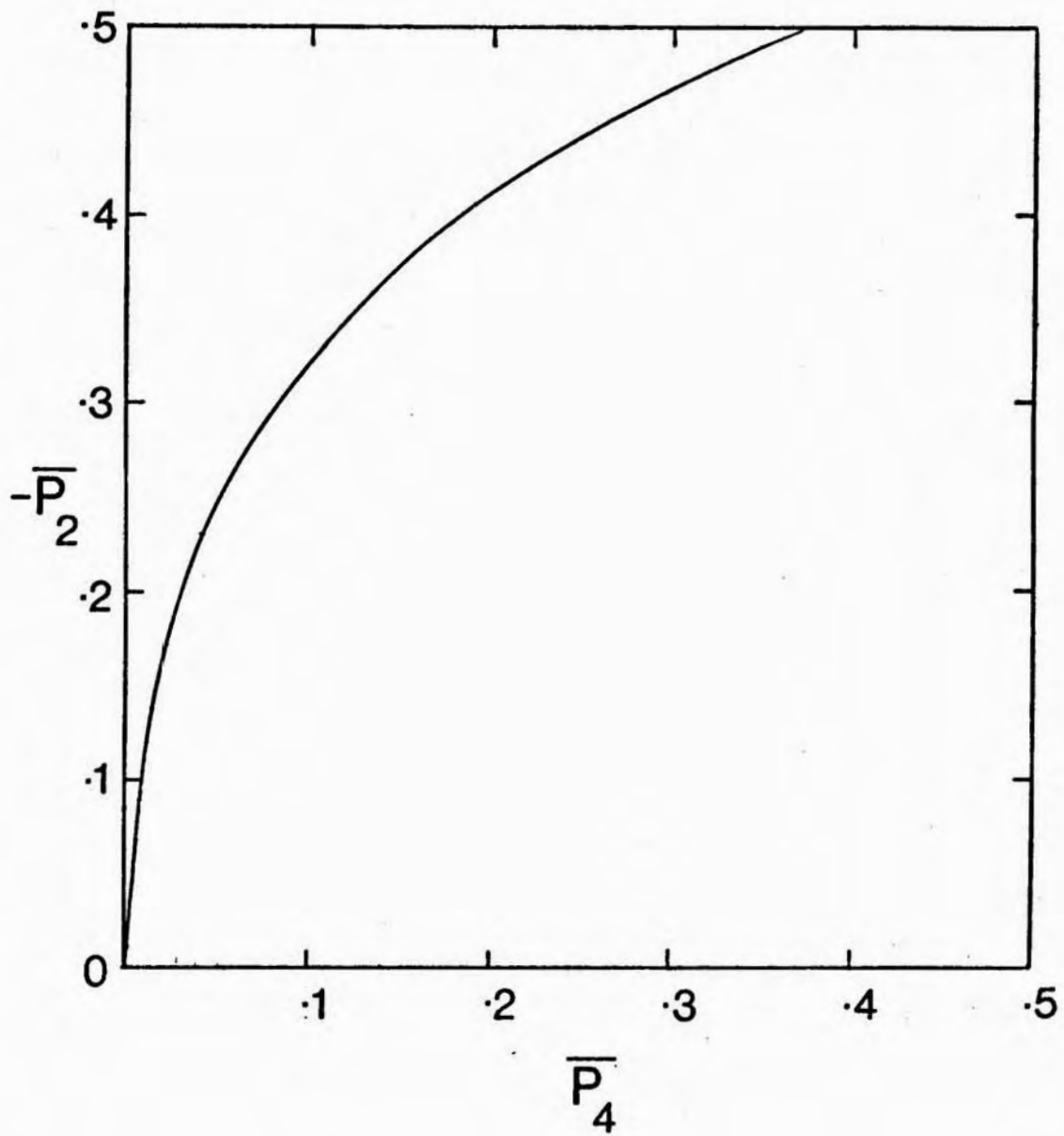


Figure 2.4 The relation between the order parameters $\bar{P}_2$ and $\bar{P}_4$ according to the Maier-Saupe model, for negative $\bar{P}_2$.

2.4 The Nematic - Isotropic Phase Transition

In the previous section we have studied the order parameter $\bar{P}_2$, defined by equation (2.52), as a function of the interaction parameter ξ . We have seen that $\bar{P}_2(\xi)$ is a continuous and differentiable function that vanishes only when $\xi=0$. It is apparent that we cannot just look at its graph (figure 2.2) to locate where the nematic-isotropic transition occurs. What we should do instead is to remember (c.f. Chapter 1) that a first order transition occurs when the slope of the free energy of the system has a discontinuity. Since we calculate only the orientational contribution to the thermodynamical quantities we can equivalently say that the nematic-isotropic phase transition occurs when the free energy of the mesophase becomes higher than the free energy of the isotropic reference state, which is just taken as zero. In figure 2.5 we plot the orientational free energy of the Maier-Saupe like model (continuous line). It is now clear from this figure that a phase transition does indeed occur when $\xi=\xi_k = 2.903$, since there the curve crosses the abscissa. Remembering that $\xi = -u_2 \bar{P}_2 / kT$ and noticing $\bar{P}_2$ at this point is 0.43, we obtain that

$$\alpha_K \equiv (-u_2 / kT_K) = 4.541,$$

where T_K is the transition temperature. The transition is of first order, since the slope of the free energy, when it crosses the abscissa, is not zero, and at that point the order parameter jumps discontinuously to zero. The peak in the free energy at $\xi=2.2$ correspond physically to the maximum temperature, T' , at which the mesophase can be thermodynamically stable, even if it is unfavoured as compared to the isotropic phase since $T > T_K$. For $T > T'$ the mesophase is absolutely unstable (81): T' represents the superheating limit of the mesophase.

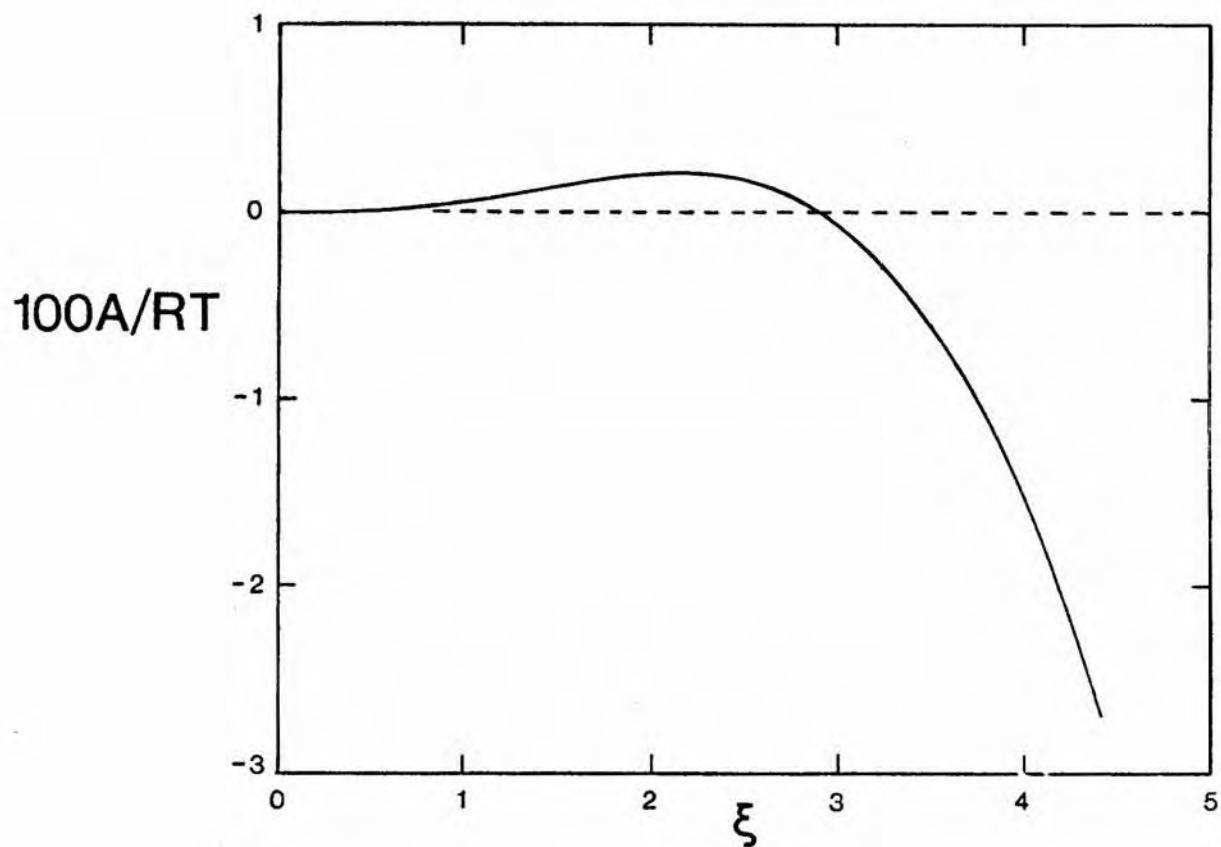


Figure 2.5 The orientational molar free energy for the Maier-Saupe model. The continuous line is the free energy of the hypothetical mesophase and the dashed line that of the disordered reference state.

CHAPTER THREE

A MOLECULAR FIELD THEORY FOR UNIAXIAL NEMATIC LIQUID CRYSTALS FORMED BY NON-CYLINDRICALLY SYMMETRIC MOLECULES

3.1 Introduction

An essential characteristic of compounds forming liquid crystals is the rod-like shape of their constituent molecules, with an attendant high length to breadth ratio. This common feature has prompted both experimentalist and theoreticians to suppose that the molecules possess cylindrical symmetry; an assumption which has many attractions. For example, the ordering matrix, often used to describe the partial alignment in a mesophase, contains just one independent element and this can be determined by a variety of techniques (43,49). The assumption of molecular cylindrical symmetry is appealing to a statistical mechanician because the pairwise anisotropic intermolecular potential required in any calculation is particularly simple for such particles (66). However, the molecules forming liquid crystals are, in fact lath-like and certainly do not possess the high symmetry which is frequently assumed for them.

Two principal components of the ordering matrix are therefore required to describe the orientational order of a uniaxial mesophase composed of lath-like molecules although most investigators are content to assume that one is sufficient. However Alben et al. (82) have estimated the ordering matrix for 4,4'-dimethoxyazoxybenzene and find the deviation of this matrix from cylindrical symmetry to be significant. Their analysis is open to question (83) and it is regrettable that

there have been no further attempts to determine the entire ordering matrix for real nematogens. Fortunately the importance of deviations from cylindrical symmetry may be inferred from unambiguous determinations of the ordering matrix for rodlike molecules, such as 4,4'-dichlorobiphenyl (84), dissolved in a nematic mesophase. In addition these matrices are found to be comparable to that estimated by Alben et al. for a pure mesophase.

In unusual contrast to the experimentalists, theoreticians have been more concerned with exploring the consequences of deviations from molecular cylindrical symmetry. Thus Frieser (85) has shown that a system composed of particles with a lower symmetry than $D_{\infty h}$ is capable of existing either as a uniaxial or a biaxial liquid crystal. The possible existence of a biaxial phase has been studied in some detail for a system of hard rectangular plates using a lattice model (86), the Landau approach (87) and the molecular field approximation (88). These calculations confirm the original prediction of the eventual transition to a biaxial phase although this transition has yet to be discovered. Indeed, all known nematics are uniaxial so presumably the mesophase freezes before the predicted transition to the biaxial phase can occur. None-the-less although deviations from molecular cylindrical symmetry have yet to be evidenced by the observation of a biaxial phase such deviations should influence the order parameters for the liquid crystal in the uniaxial phase. For example, the deviation of the ordering matrix from cylindrical symmetry is clearly determined by the molecular symmetry and the element of the intermolecular potential. Straley (88) has reported calculations of the ordering matrix for an ensemble of hard rectangular particles. These calcula-

tions are of some interest but they may not be particularly realistic, especially as recent experiments have indicated that dispersion forces may make a dominant contribution to the anisotropic intermolecular potential (89). In this Chapter therefore we shall develop, within the molecular field approximation, a theory for non-cylindrically symmetric particles interacting via a completely general intermolecular potential. We then obtain a series expansion for the orientational pseudo-potential in the uniaxial phase. The expansion coefficients are subsequently determined by assuming that dispersion forces make the only contribution to the anisotropic intermolecular potential. We are then able to investigate the influence of deviations from molecular cylindrical symmetry on the nematic-isotropic transition and the various order parameters. Finally we compare these predictions with the data available for the nematogen 4,4'-dimethoxyazoxybenzene.

3.2 The orientational Pseudo-Potential

As we have seen in the previous Chapter the simple procedure employed by Humphries, James and Luckhurst (33) to obtain the orientational pseudo-potential yields the same results, at the first level of approximation, as a more rigorous approach based on the factorization of the total partition function. For the sake of simplicity we shall then use in this Chapter the H-J-L procedure, which amounts to taking three averages of the intermolecular potential. The first of these is over all orientations of the intermolecular vector, the second over all orientations of one particle and finally over the intermolecular separation.

We begin with the intermolecular potential which, for particles of general shape, we expand in a product basis of Wigner rotation matrices (34) as

$$U_{12} = \sum_{L_1 L_2 m_1 m_2 n_1 n_2} (R_{12}) D_{m_1, n_1}^{L_1}(\Omega_{1-R}) D_{m_2, n_2}^{L_2}(\Omega_{2-R}), \quad (3.1)$$

where R_{12} is the separation between molecules 1 and 2 (67). The orientation of molecule i in a coordinate system containing the intermolecular vector as the z axis is denoted by Ω_{i-R} . The energy U_{12} is clearly invariant under rotation of the coordinate system about this z axis and so we restrict the summation to those terms with m_1 equal to $-m_2$ (67):

$$U_{12} = \sum_{L_1 L_2 m n_1 n_2} (R_{12}) D_{m, n_1}^{L_1}(\Omega_{1-R}) D_{-m, n_2}^{L_2}(\Omega_{2-R}); \quad (3.2)$$

where $u_{L_1 L_2 m n_1 n_2} \equiv u_{L_1 L_2 m -m n_1 n_2}$.

It is convenient to define the molecular orientation in terms of a common coordinate system and so we transform the potential U_{12} to a laboratory frame. The choice of this coordinate system is determined by the symmetry of the liquid crystal phase and for a uniaxial mesophase we shall take the laboratory z-axis to be parallel to the symmetry axis of the mesophase i.e. to the director. The transformation of U_{12} is carried out by performing the rotation from the intermolecular vector to the molecule in two steps using the relationship

$$D_{m,n}^L(\Omega_{1-R}) = \sum_q D_{q,m}^{L*}(\Omega_{R-L}) D_{q,n}^L(\Omega_{1-L}). \quad (3.3)$$

Here the subscript R-L denotes the rotation from the laboratory to the intermolecular frame while 1-L indicates that from the laboratory to the molecule coordinate system. The intermolecular potential becomes

$$U_{12} = \sum_{L_1 L_2 m m_1 n_2} u_{L_1 L_2 m m_1 n_2} (R_{12}) D_{q_1, n_1}^{L_1}(\Omega_{1-L}) D_{q_2, n_2}^{L_2}(\Omega_{2-L}) D_{q_1, m}^{L_1*}(\Omega_{R-L}) D_{q_2, -m}^{L_2*}(\Omega_{R-L}), \quad (3.4)$$

and we may now take the average over the orientation of the intermolecular vector. If the distribution function for the intermolecular vector is orientation independent (see the discussion in Section 2.2) then we may take advantage of the orthogonality of the rotation matrices to evaluate the ensemble average $\overline{D_{q_1, m}^{L_1*}(\Omega_{R-L}) D_{q_2, -m}^{L_2*}(\Omega_{R-L})}$ as

$$D_{q_1, m}^{L_1*}(\Omega_{R-L}) D_{q_2, -m}^{L_2*}(\Omega_{R-L}) = (-1)^{q_2+m} \delta_{q_1, -q_2} \delta_{L_1, L_2} / (2L_1+1). \quad (3.5)$$

The partially averaged potential may then be written as

$$U_{12} = \int \frac{(-1)^{q+m}}{(2L+1)} u_{LLmm_1n_2}(R_{12}) D_{q, n_1}^L(\Omega_{1-L}) D_{-q, n_2}^L(\Omega_{2-L}). \quad (3.6)$$

The next stage is to average over the orientations adopted by particle 2 and so we require $\overline{D_{-q, n_2}^L}$. Within the molecular field approximation this average is taken to be independent of the orientation of molecule 1 and is to be identified with the normal ensemble average. Since we are only concerned with a $D_{\infty h}$ uniaxial mesophase the average $\overline{D_{-q, n_2}^L}$ will vanish unless q is zero and L is even. The potential is now reduced to

$$U_{12} = \int' \frac{(-1)^m}{(2L+1)} u_{LLmm_1n_2}(R_{12}) \overline{D_{0, n_2}^L} D_{0, n_1}^L(\Omega_{1-L}); \quad (3.7)$$

where the prime denotes a summation restricted to even values of L greater than zero. The scalar contribution to the potential is ignored because we are only concerned with the orientational properties of the mesophase. The final average is over all intermolecular separations and gives the orientational pseudo-potential, for molecule 1, as

$$U_1 = \int' \frac{(-1)^m}{(2L+1)} \bar{u}_{LLmm_1n_2} \overline{D_{0, n_2}^L} D_{0, n_1}^L(\Omega_{1-L}). \quad (3.8)$$

The expansion coefficients are defined by

$$\bar{u}_{LLmm_1n_2} = \frac{\int u_{LLmm_1n_2}(R_{12}) \exp\{-U_S(R_1 \dots R_N)/kT\} d^3R_1 d^3R_2 d^3R_3 \dots d^3R_N}{\int \exp\{-U_S(R_1 \dots R_N)/kT\} d^3R_1 \dots d^3R_N} \quad (3.9)$$

where $U_S(R_1 \dots R_N)$ is the scalar potential of the N molecules in the ensemble (c.f. Chapter 2). The pseudo-potential is conveniently written as

$$U(\beta\gamma) = \sum' u_{Lqp} \overline{D_{0,p}^L} D_{0,q}^L(\beta\gamma), \quad (3.10)$$

where

$$u_{Lqp} = \sum_m (-1)^m \overline{u_{Lmqp}} / (2L+1);$$

the Euler angles (β, γ) define the orientation of the director in the molecular coordinate system.

We have three checks on this form of the pseudo-potential. The first occurs for an ensemble of cylindrically symmetric molecules for then the summation in equation (3.2) for the pairwise intermolecular potential is restricted to terms for which both n_1 and n_2 are zero as we assumed in the previous chapter. With these restrictions the pseudo-potential, given in equation (3.10), reduces to

$$U(\beta) = \sum' u_{L00} \overline{P_L} P_L(\cos\beta), \quad (3.11)$$

in complete agreement with the result derived by Humphries, James and Luckhurst (33). The second particular case is an infinitely dilute solution of molecules of arbitrary shape in a liquid of cylindrically symmetric particles. The orientational pseudo-potential for the non-cylindrically symmetric molecule in such a system is obtained formally from equation (3.10) by setting p equal to zero and yielding

$$U(\beta\gamma) = \sum' u_{Lq0} \bar{P}_L^D D_{0,q}^L(\beta\gamma), \quad (3.12)$$

in accord with the result obtained by Humphries and Luckhurst (90). Finally if the summation in equation (3.10) is restricted to terms with L equal to 2, then the pseudo-potential is identical in form to that proposed by Straley on the basis of symmetry arguments (88).

We conclude this section by considering the symmetry properties of the coefficients u_{Lqp} . For identical particles the permutation symmetry of the pairwise intermolecular potential ensures that (67)

$$u_{L_1 L_2 m_1 n_2}(R_{12}) = (-1)^{L_1+L_2} u_{L_2 L_1 -m_2 n_1}(R_{12}), \quad (3.13)$$

and so

$$u_{Lqp} = u_{Lpq}. \quad (3.14)$$

The pair potential must also be real and this requires that

$$u_{L_1 L_2 m_1 n_2}(R_{12}) = (-1)^{n_1+n_2} u_{L_1 L_2 -m_1 -n_2}(R_{12})^*; \quad (3.15)$$

consequently

$$u_{Lqp} = (-1)^{q+p} u_{L-q-p}^*. \quad (3.16)$$

3.3 Parameterisation

One of our major objectives is to investigate the influence of deviations from molecular cylindrical symmetry on the various orientational order parameters for a uniaxial nematic mesophase. We therefore seek to minimise the number of variables in the calculation while maintaining the essential physics. As a first approximation we shall consider only those terms with L equal to 2 in the expansion of the pseudo-potential. We expect the neglect of terms higher than quadratic to be a realistic approximation since similar assumptions for cylindrically symmetric particles have led to results in reasonable agreement with experiment (32,33). We can reduce the number of expansion coefficients still further by appealing to some specific model for the interactions or by imposing symmetry restrictions on the molecules. For example if we follow Straley (88) and take the particles to be hard rectangular parallelopipeds then the coefficients u_{2qp} are independent of the sign of either p or q and zero if either of these subscripts is odd. In fact

$$u_{200} = \{-2B(W^2+L^2) - 2W(L^2+B^2) + L(W^2+B^2) + 8WBL\}/3, \quad (3.17)$$

$$u_{220} = (L^2-BW)(B-W)/\sqrt{6}, \quad (3.18)$$

and

$$u_{222} = -L(W-B)^2/2, \quad (3.19)$$

where L is the length, B the breadth and W the width of the particle. This particular parameterisation is only approximate (88) and in

addition anisotropic repulsive forces are probably not dominant in determining the behaviour of real liquid crystals. We have therefore derived expressions for the u_{2qp} for molecules interacting via dispersion forces and, as we show in Section 3.3(b) these coefficients again vanish if either p or q is odd and are also independent of the sign of p or q .

It is possible to place similar restrictions on the expansion coefficients u_{Lqp} , without appealing to specific forms of the inter-molecular interactions, by using more formal arguments based on the molecular symmetry and its influence on the pair potential. For example if each molecule has a centre of symmetry then (67)

$$\begin{aligned} u_{L_1 L_2 m n_1 n_2}^{(R_{12})} &= (-1)^{L_1 - n_1} u_{L_1 L_2 m - n_1 n_2}^{(R_{12})} \\ &= (-1)^{L_2 - n_2} u_{L_1 L_2 m n_1 - n_2}^{(R_{12})} \\ &= (-1)^{L_1 + L_2 - n_1 - n_2} u_{L_1 L_2 m - n_1 - n_2}^{(R_{12})}; \end{aligned} \quad (3.20)$$

consequently

$$u_{Lqp} = (-1)^q u_{L-qp} = (-1)^p u_{Lq-p} = (-1)^{q+p} u_{L-q-p} \quad (3.21)$$

but for this to be compatible with equation (3.16) the coefficients must be real. Further, if the molecules also possess a plane of symmetry orthogonal to their z -axes then

$$\begin{aligned} u_{L_1 L_2 m n_1 n_2}^{(R_{12})} &= (-1)^{L_1} u_{L_1 L_2 m - n_1 n_2}^{(R_{12})} = (-1)^{L_2} u_{L_1 L_2 m n_1 - n_2}^{(R_{12})} \\ &= (-1)^{L_1 + L_2} u_{L_1 L_2 m - n_1 - n_2}^{(R_{12})} \end{aligned} \quad (3.22)$$

and so

$$u_{Lqp} = (-1)^L u_{Lq-p} = u_{L-q-p} = u_{L-q-p} \quad (3.23)$$

However, equations (3.21) and (3.23) can only be consistent if both p and q are restricted to even values; in addition the coefficients are independent of the sign of p and q .

Given these general restrictions on the coefficients u_{Lqp} we may write the pseudo-potential as

$$U(\beta\gamma) = \sum_{\substack{L, |p|, |q| \\ (\text{even})}} u_{Lqp} \{ \overline{D_{0,p}^L} + \overline{D_{0,-p}^L} \} \{ D_{0,q}^L(\beta\gamma) + D_{0,-q}^L(\beta\gamma) \} /$$

$$(1 + \delta_{0q})(1 + \delta_{0p}). \quad (3.24)$$

If we now limit the summation to those terms with L equal to 2 we have

$$U(\beta\gamma) = \{ u_{200} \overline{d_{0,0}^2} + 2u_{220} \overline{d_{02}^2 \cos 2\gamma} \} d_{0,0}^2(\beta)$$

$$+ \{ 2 u_{200} \overline{d_{0,0}^2} + 4u_{222} \overline{d_{0,2}^2 \cos 2\gamma} \} d_{0,2}^2(\beta) \cos 2\gamma, \quad (3.25)$$

where $d_{m,n}^2(\beta)$ is a reduced Wigner rotation matrix (34). The second rank order parameters $\overline{d_{0,0}^2}$ and $\overline{d_{0,2}^2 \cos 2\gamma}$ occurring in this expression are directly related to the principal elements of the ordering matrix (c.f. equations 1.9). In particular

$$S_{zz} = \overline{d_{0,0}^2}, \quad (3.26)$$

and

$$S_{xx} - S_{yy} = \sqrt{6} \overline{d_{0,2}^2} \cos 2\gamma. \quad (3.27)$$

We see therefore that the order parameter $\overline{d_{0,2}^2} \cos 2\gamma$ reflects the deviation of the ordering matrix from cylindrical symmetry. Other order parameters have been introduced to measure the deviation of the ordering matrix from cylindrical symmetry although they only differ by simple numerical factors; thus Alben et al. (82) use the symbol D to denote $\sqrt{6} \overline{d_{0,2}^2} \cos 2\gamma$ while Straley (88) has chosen U which is equivalent to $\sqrt{8/3} \overline{d_{0,2}^2} \cos 2\gamma$. For calculations it is convenient to write the pseudo-potential as

$$U(\beta\gamma) = -kT \{a \overline{d_{0,0}^2}(\beta) + b \overline{d_{0,2}^2}(\beta) \cos 2\gamma\}, \quad (3.28)$$

where

$$a = - \{u_{200} \overline{d_{0,0}^2} + 2u_{220} \overline{d_{0,2}^2} \cos 2\gamma\} / kT, \quad (3.29)$$

and

$$b = - \{2u_{220} \overline{d_{0,0}^2} + 4u_{222} \overline{d_{0,2}^2} \cos 2\gamma\} / kT. \quad (3.30)$$

The pseudo-partition function for this single particle potential is then

$$\begin{aligned} Z(a,b) &= \int_0^{2\pi} \int_0^\pi \exp\{a \overline{d_{0,0}^2}(\beta) + b \overline{d_{0,2}^2}(\beta) \cos 2\gamma\} \sin\beta d\beta d\gamma, \\ &= 2\pi \int_0^\pi I_0 \{(b \overline{d_{0,2}^2}(\beta))\} \exp\{a \overline{d_{0,0}^2}(\beta)\} \sin\beta d\beta, \end{aligned} \quad (3.31)$$

where $I_n(x)$ is an nth order modified Bessel function (80). The orientational molar potential energy U is just one half the total average energy $\bar{U}$ (33),

$$U = -(RT/2) (a \overline{d_{0,0}^2} + b \overline{d_{0,2}^2 \cos 2\gamma}), \quad (3.32)$$

the molar entropy S is

$$S = -R (a \overline{d_{0,0}^2} + b \overline{d_{0,2}^2 \cos 2\gamma}) + R \ln Z(a,b), \quad (3.33)$$

and so the orientational molar Helmholtz function is

$$A_m = (RT/2) (a \overline{d_{0,0}^2} + b \overline{d_{0,2}^2 \cos 2\gamma}) - RT \ln Z(a,b) \quad (3.34)$$

This free energy will be a minimum provided the consistency equations for the order parameters

$$\begin{aligned} \overline{d_{0,0}^2} &= \int_0^{2\pi} \int_0^\pi d_{0,0}^2(\beta) \exp\{a d_{0,0}^2(\beta) + b d_{0,2}^2(\beta) \cos 2\gamma\} \sin \beta d\beta d\gamma / Z(a,b) \\ &= 2\pi \int_0^\pi d_{0,0}^2(\beta) I_0\{b d_{0,2}^2(\beta)\} \exp\{a d_{0,0}^2(\beta)\} \sin \beta d\beta / Z(a,b), \end{aligned} \quad (3.35)$$

and

$$\begin{aligned} \overline{d_{0,2}^2 \cos 2\gamma} &= \int_0^{2\pi} \int_0^\pi d_{0,2}^2(\beta) \cos 2\gamma \exp\{a d_{0,0}^2(\beta) + b d_{0,2}^2(\beta) \cos 2\gamma\} \\ &\quad \sin \beta d\beta d\gamma / Z(a,b), \\ &= 2\pi \int_0^\pi d_{0,2}^2(\beta) I_1\{b d_{0,2}^2(\beta)\} \exp\{a d_{0,0}^2(\beta)\} \sin \beta d\beta / Z(a,b), \end{aligned} \quad (3.36)$$

are satisfied.

The two consistency equations may be solved in a variety of ways. For example we might first fix the three variables u_{200}/kT , u_{220}/kT and u_{222}/kT and then evaluate the integrals in equations (3.35) and (3.36) for trial values of the order parameters $\overline{d_{0,0}^2}$ and $\overline{d_{0,2}^2 \cos 2\gamma}$. The trial values would then be varied, using a non-linear least squares fitting routine (33), until the consistency conditions are satisfied. An alternative, and often more convenient approach, is to tabulate the order parameters and thermodynamic functions for a range of values of the variables a and b . The ratios u_{220}/u_{200} and u_{222}/u_{200} of the expansion coefficients may then be extracted from the variables with the aid of equations (3.29) and (3.30). This exercise is particularly straightforward when the particles interact via dispersion forces because the ratio u_{222}/u_{200} is just $(u_{220}/u_{200})^2$ as we shall now show.

Section 3.3(b) Parameterisation for Dispersion Forces

Here we derive expressions for the expansion coefficients $u_{L_1 L_2 m_1 m_2}^{(R_{12})}$ when the molecules interact via dispersion forces (91). Our starting point is the dispersion interaction energy for a pair of molecules in their electronic ground states (92),

$$U_{12} = d_{12} A_{\alpha\delta} B_{\alpha\delta}, \quad (3.37)$$

where the tensor convention of summation over repeated Greek subscripts is adopted. The proportionality constant d_{12} is given by

$$d_{12} = -\epsilon_1 \epsilon_2 / (\epsilon_1 + \epsilon_2), \quad (3.38)$$

where ϵ_i is an energy parameter often identified with an ionization

potential. The tensors A and B are defined in terms of the polarizability tensors α_1 and α_2 , for the two molecules, by

$$A_{\alpha\delta} = \nabla_{\alpha} \nabla_{\beta} (1/R_{12}) \alpha_{2\beta\delta}, \quad (3.39)$$

and

$$B_{\alpha\delta} = \alpha_{1\alpha\gamma} \nabla_{\gamma} \nabla_{\delta} (1/R_{12}). \quad (3.40)$$

The scalar product in equation (3.37) may also be written in irreducible spherical tensor form (34) as

$$U_{12} = d_{12} \sum_{L,m} A^{(L,m)} B^{(L,m)*}. \quad (3.41)$$

where L may only take values 0, 1 and 2 because A and B are second rank tensors. The irreducible components $A^{(L,m)}$ are constructed from the tensors T and α according to the prescription (91b)

$$A^{(L,m)} = (-1)^{L+1} \sum_{\substack{L_1 L_2 \\ q}} \{ (2L_1+1)(2L_2+1) \}^{\frac{1}{2}} W(L_1 L_1 1 L) C(L_2 L_1 L; m-q, q) \\ \times T^{(L_1, q)} \alpha_2^{(L_2, m-q)}, \quad (3.42)$$

where $W(abcd;ef)$ and $C(abc;de)$ are Racah and Clebsch-Gordan coefficients respectively (34). The values of L_1 and q may be restricted by working in a coordinate system containing the intermolecular vector as z -axis; in this case the only non-vanishing

component is

$$T^{(2,0)} = \sqrt{3/2} T_{zz} = \sqrt{6}/R_{12}^3.$$

The same restrictions hold for $B^{(L,m)}$ and so

$$U_{12} = \sum_{\substack{L_1 L_2 \\ m}} \zeta_{L_1 L_2 m}(R_{12}) \alpha_1^{(L_1, m)*} \alpha_2^{(L_2, m)}, \quad (3.43)$$

where

$$\begin{aligned} \zeta_{L_1 L_2 m}(R_{12}) = \frac{30}{R_{12}^6} d_{12} \{ (2L_1+1)(2L_2+1) \}^{\frac{1}{2}} \sum_L W(L_2 1 2 1; 1 L) W(2 1 L_1; 1 L) \\ \times C(2 L_1 L; 0 m) C(L_2 2 L; m 0) \end{aligned} \quad (3.44)$$

Transforming the polarizability tensors to their respective molecular coordinate system gives the dispersion energy as

$$\begin{aligned} U_{12} = \sum \{ (-1)^{m-n_1-n_2} \zeta_{L_1 L_2 m}(R_{12}) \alpha_1^{(L_1, n_1)*} \alpha_2^{(L_2, n_2)*} \} D_{m, n_1}^{L_1}(\Omega_{1-R}) \\ D_{-m, n_2}^{L_2}(\Omega_{2-R}) \end{aligned} \quad (3.45)$$

This result has the same form as the general expansion of the pairwise intermolecular potential given in equation (3.2) and allows us to identify the coefficients in that expansion as

$$u_{L_1 L_2 m n_1 n_2}(R_{12}) = (-1)^{m-n_1-n_2} \zeta_{L_1 L_2 m}(R_{12}) \alpha_1^{(L_1, n_1)*} \alpha_2^{(L_2, n_2)*}; \quad (3.46)$$

of course L_1 and L_2 may only take values 0 or 2 because the polarizability α is a symmetric second rank tensor. Consequently the surviving coefficients u_{Lqp} are found to be

$$u_{2qp} = d_{12} \alpha^{(2,q)} \alpha^{(2,p)} / 5 \overline{R_{12}^6}, \quad (3.47)$$

after evaluating the vector coupling coefficients.

Equations (3.29) and (3.30) now become

$$a = -\alpha \{ \overline{d_{0,0}^2} + 2\lambda \overline{d_{0,2}^2} \cos 2\gamma \}, \quad (3.48)$$

and

$$b = 2\lambda a \quad (3.49)$$

where

$$\alpha = -u_{200}/kT; \quad (3.50)$$

and λ is the ratio u_{220}/u_{200} .

We may therefore fix the parameter λ , which is a measure of the deviation from cylindrical symmetry, at the start of the calculation and from the results, tabulated simply as a function of α , obtain the behaviour of the ensemble as the temperature is varied. In the next section we shall describe the results of such calculations and compare these theoretical predictions with experiment. For this final section we shall denote the order $\overline{d_{0,0}^2}$ by the more usual $\overline{P_2}$ and the secondary parameter $\overline{d_{0,2}^2} \cos 2\gamma$ by $\overline{D_{0,2}^2}$.

3.4 Predictions and Reality

The first stage in the calculation is the identification of the transition from the isotropic phase to the uniaxial nematic phase. This may be accomplished for a given molecular asymmetry by determining the value of α at which the orientational Helmholtz function vanishes, provided of course there is no volume change at the transition. The value, α_K is then related to the transition temperature T_K by

$$\alpha_K = -u_{200}/kT_K. \quad (3.51)$$

The results of such calculations are listed in Table 3.1 for a range of λ values including $\lambda=0$ which corresponds to the Maier-Saupe limit for cylindrically symmetric particles. We can see immediately that increasing the deviation from cylindrical symmetry decreases α_K and so increases the nematic-isotropic transition temperature for constant u_{200} . At first sight this trend is somewhat surprising although it is in accord with calculations based on a quite different model (88). To appreciate the

Table 3.1 The order parameters and entropy at the nematic-isotropic transition.

λ	α_K	$P_2^{(K)}$	$D_{0,2}^{2(K)}$	$P_4^{(K)}$	$S^{(K)}/R$
0	4.541	0.429	0	0.120	0.417
0.1	4.505	0.408	0.017	0.109	0.384
0.2	4.386	0.341	0.035	0.075	0.275
0.3	4.160	0.207	0.041	0.029	0.112

origin of this effect it is important to realise that varying λ while holding u_{200} fixed corresponds to keeping the component α'_{zz} of the traceless polarizability tensor constant, increasing α'_{xx} by a given amount and decreasing α'_{yy} by the same amount. Under these conditions the orientational energy of a pair of particles, with parallel principal co-ordinate systems, becomes more negative as the deviation from cylindrical symmetry increases. It is this stabilization of the parallel configuration which is responsible for the increased range of the nematic mesophase.

The values of several order parameters, at the transition temperature, are also given in the table. The parameter $\bar{P}_2^{(K)}$ is seen to decrease with increasing λ , a behaviour which might appear to be incompatible with the greater tendency for parallel molecular alignment. However, in the limit that the components α'_{zz} and α'_{xx} of the traceless polarizability tensor become identical, as for a disc-like particle, it is the y-axis which will tend to be parallel to the director. Consequently the z-axis will tend to be orthogonal to the director and $\bar{P}_2$ will be small or even negative; the order parameter $\bar{P}_2$ must therefore decrease with increasing deviation from cylindrical symmetry so as to approach this limit. Similar arguments hold for the higher parameter $\bar{P}_4^{(K)}$ as λ is increased. In contrast the order parameter $\bar{D}_{0,2}^{2(K)}$ which reflects the deviation from cylindrical symmetry, shows the expected increase with increasing λ . Finally, the entropy change at the order-disorder transition, also listed in the table, decreases with increasing λ , in accord with the decrease in $\bar{P}_2^{(K)}$.

The temperature dependence of the order parameters $\bar{P}_2$ and $\bar{P}_4$

for the long molecular axis is shown in figure 3.1 for several values of λ . The results are plotted as a function of the reduced variable $(\alpha/\alpha_K)^{-1}$ which is identical to the reduced temperature T/T_K provided the coefficients u_{2qp} are themselves independent of temperature. The lines labelled $\lambda=0$ correspond to the Maier-Saupe limit and the effect of introducing deviations from cylindrical symmetry is to lower these curves as well as changing their slopes. The order parameter $\bar{P}_4$ is found to be positive for all reasonable values of λ and so deviations from cylindrical symmetry cannot be invoked as an explanation for the negative values of $\bar{P}_4$ determined for 4-n-butyloxybenzylidene-4'-cyano aniline dissolved in 4-methoxybenzylidene-4'-n-butylaniline (51). The secondary order parameter $\overline{D_{0,2}^2}$ is plotted as a function of $\bar{P}_2$ in figure 3.2 for various λ values. These results exhibit an unusual behaviour for the order parameter $\overline{D_{0,2}^2}$ is observed to increase with increasing $\bar{P}_2$ pass through a maximum and then decrease, going finally to zero when the z-axis is completely ordered. The temperature dependence of the secondary order parameter $\overline{D_{0,2}^2}$ is shown in figure 3.3 for some values of λ .

We now turn to a detailed comparison of these predictions with experiment. The most direct evidence for the influence of deviations from molecular cylindrical symmetry on the behaviour of the mesophase is the observation of the secondary order parameter $\overline{D_{0,2}^2}$ because this is identically zero for cylindrically symmetric particles. Of course the other order parameters will also depart from their Maier-Saupe values but similar deviations may also be observed for cylindrically symmetric particles if quadratic and quartic terms are retained in the pseudo-potential given by equation (3.11) (33,93). Unfortunately the

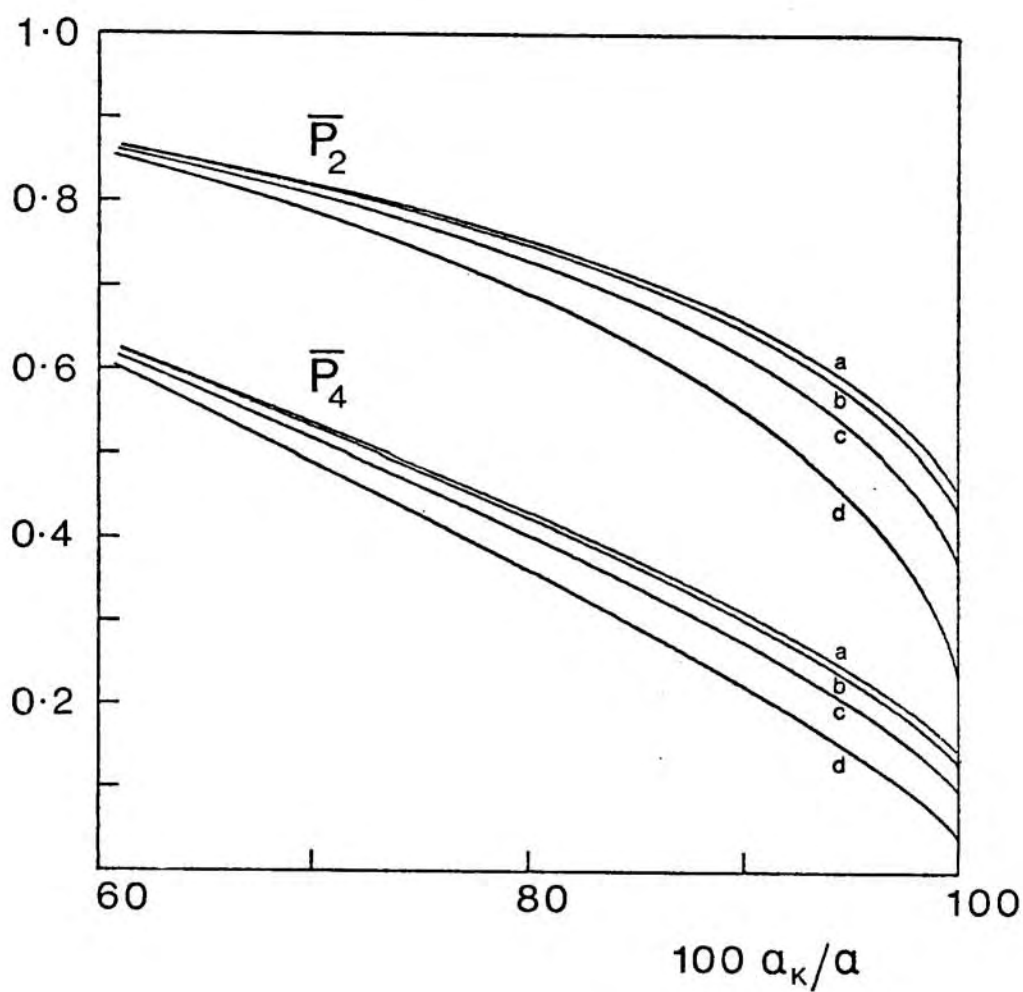


Figure 3.1 The dependence of the order parameters $\bar{P}_2$ and $\bar{P}_4$ on the reduced variable α/α_K for λ equal to (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3.

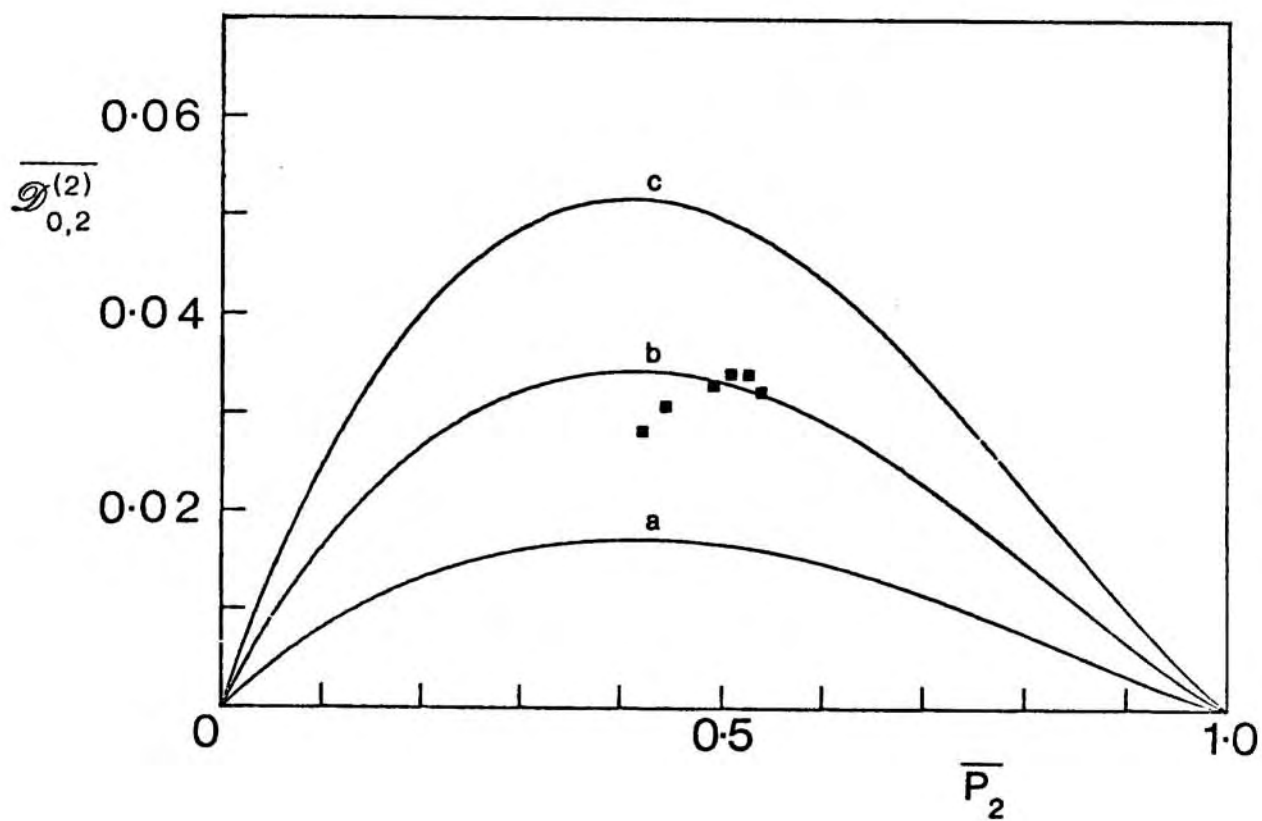


Figure 3.2 The variation of the secondary order parameter $\overline{D_{0,2}^{(2)}}$ with the order parameter $\overline{P_2}$ calculated for λ equal to (a) 0.1, (b) 0.2 and (c) 0.3.

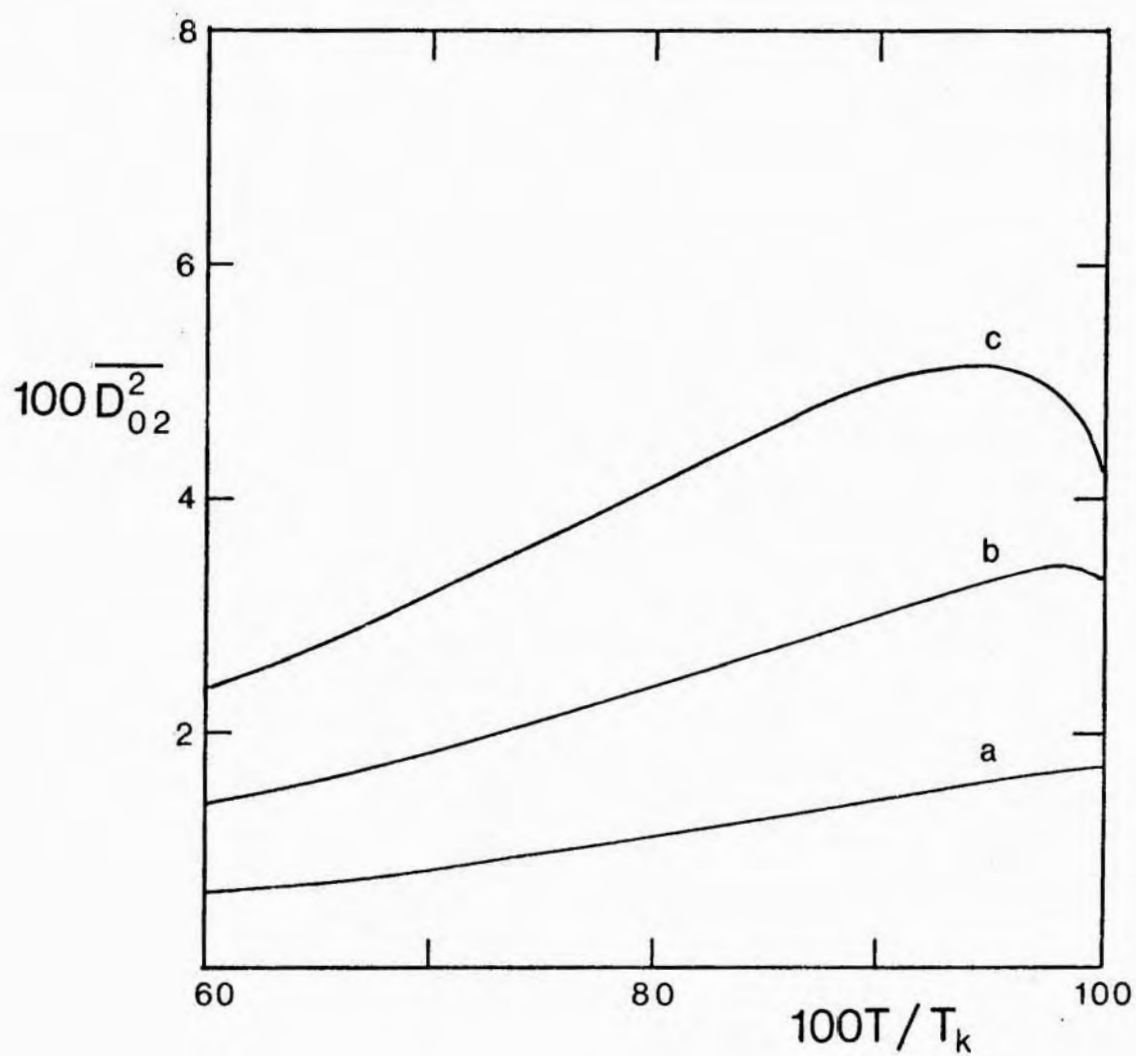


Figure 3.3 The temperature dependence of the secondary order parameter $\overline{D_{0,2}^2} = (S_{xx} - S_{yy})/\sqrt{6}$. The curves are calculated for λ equal to (a)0.1, (b)0.2 , (c)0.3 .

only attempt to determine $\overline{D_{0,2}^2}$ for a pure nematogen was when Alben et al. (82) showed how the nuclear magnetic resonance experiments performed by Rowell et al. (94) on partially deuterated samples of 4,4'-dimethoxyazoxybenzene might be interpreted to yield $\overline{D_{0,2}^2}$ as well as $\overline{P_2}$. Although these experiments were performed throughout the nematic range the analysis was restricted to a single temperature (82). We have therefore applied an analogous procedure to all of the data obtained by Rowell et al. (94) and found the values of $\overline{P_2}$ and $\overline{D_{0,2}^2}$ plotted in figure 3.2. The results are reasonably well accounted for by the curve obtained with λ equal to 0.2, especially as the values of $\overline{D_{0,2}^2}$ are particularly sensitive to the fine details of the geometry assumed for the nematogen. Given a λ of 0.2 we predict the entropy of transition $S^{(K)}/R$ to be 0.27 in surprisingly good agreement with the observed value of 0.28, although this does appear to ^{be} subject to some experimental uncertainty (81). This prediction is a considerable improvement on the Maier-Saupe value for $S^{(K)}/R$ of 0.42. The order parameter $\overline{P_2}$ at the transition point may also be calculated for this particular λ and we find 0.34 in good agreement with ^{the} observed value of about 0.36. This prediction should be contrasted with the Maier-Saupe value of 0.43. The higher parameter $\overline{P_4}$ is predicted to be 0.08 at the order-disorder transition but as yet there are no determinations of this quantity although it is available from light scattering experiments (50).

As a final test of the theory we compare the predicted temperature dependence of the order parameter $\overline{P_2}$ with the observed dependence. This comparison is not straightforward because the measurements are almost always made at constant pressure and as a consequence the volume will also change as the temperature is varied. The pair distribution

function employed in evaluating the average $\overline{R_{12}^{-6}}$ will then be temperature dependent and so the coefficients u_{2qp} occurring in the theory will change with temperature. It is possible to allow for this variation by assuming a simple volume dependence of the form

$$u_{2qp} = u_{2qp}^0 / V^\gamma,$$

where the u_{2qp}^0 is temperature independent (33). However, even though the temperature dependence of the volume is known, such an assumption introduces an additional variable γ into the calculation. This problem can be avoided if the order parameter is measured at constant volume for then the coefficients u_{Lqp} should, to a good approximation, be independent of temperature. Such measurements are available for 4,4'-dimethoxyazoxybenzene (61) and the order parameter $\overline{P}_2$ is plotted as a function of the reduced temperature in figure 3.4. The solid line also shown in the figure was obtained from the theory with λ set equal to 0.2. The agreement with experiment is good although the slope of the theoretical curve is slightly greater than that observed.

The theory based on deviations from cylindrical symmetry and treated within the molecular field approximation would appear to provide an acceptable account of the orientational properties of the nematogen 4,4'-dimethoxyazoxybenzene. However it is worth to recall that the same properties have been interpreted, with comparable success, by the pseudo-potential, for cylindrically symmetric particles, given by equation (3.11) with L restricted to 2 and 4 (33). The order parameter $\overline{P}_2^{(K)}$ is predicted to be 0.3, the entropy change $S^{(K)}/R$ at the transition is calculated to be 0.32 and the temperature dependence of

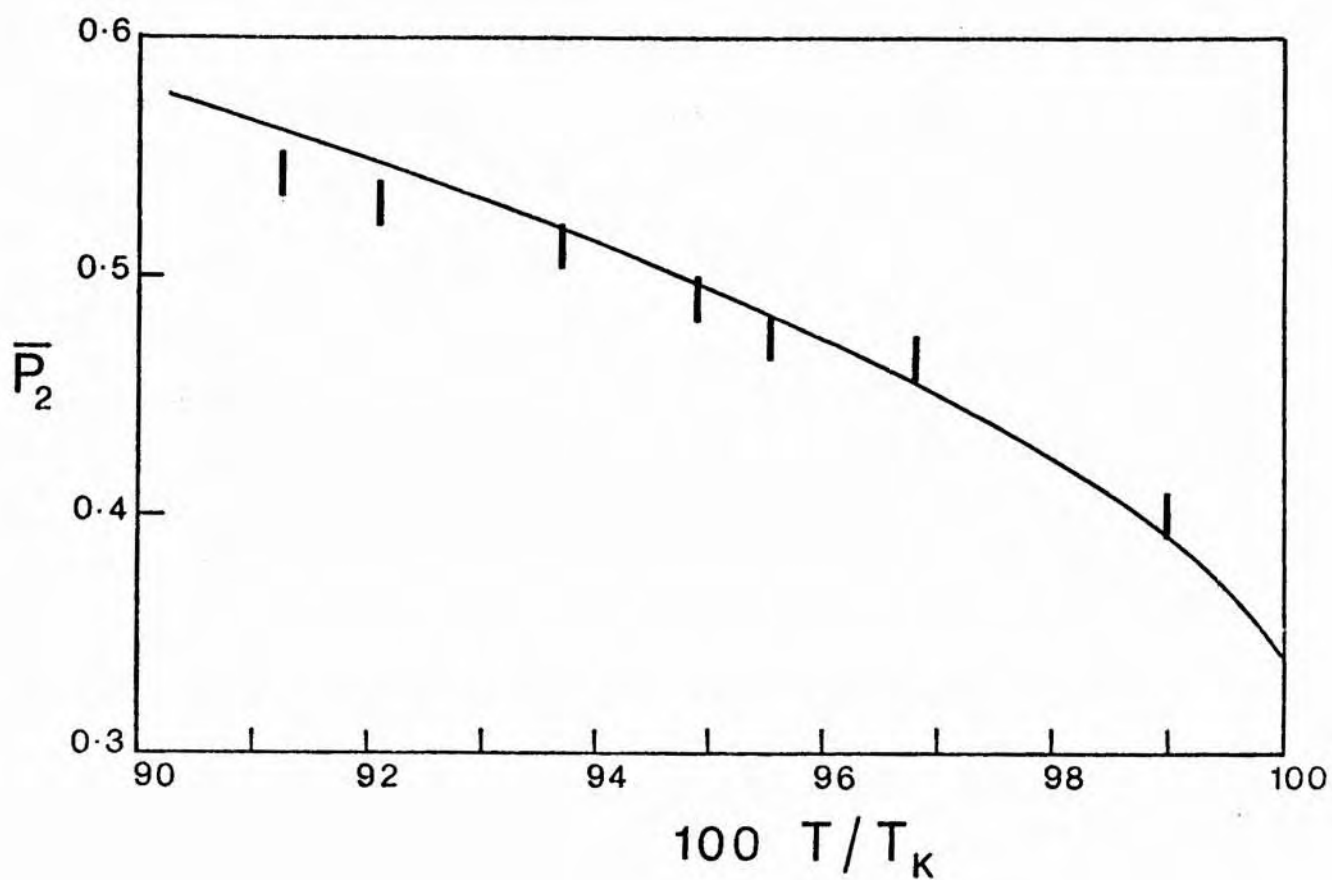


Figure 3.4 The temperature dependence of $\bar{P}_2$ observed for 4,4'-dimethoxyazoxybenzene at constant volume; the curve is calculated with λ equal to 0.2.

the order parameter $\bar{P}_2$ at constant volume is in complete accord with experiment (69). Of course the theory fails to predict the order parameter $\overline{D_{0,2}^2}$ since for cylindrically symmetric particles this must be zero. On present evidence it is hard to distinguish between the two theories although it may be significant that the parameter $\bar{P}_2^{(K)}$ is usually less than the Maier-Saupe limit (69) which is a natural result of deviations from molecular cylindrical symmetry. Clearly future experimental studies of the orientational order in nematics should concentrate on the secondary order parameter $\overline{D_{0,2}^2}$. In the event that this is shown, unambiguously, to be non-zero, then the appropriate terms must be included in the pseudo-potential. However, such observations may not exclude the retention of the quartic terms in the expansion. Indeed when $\bar{P}_2^{(K)}$ exceeds the Maier-Saupe value of 0.43, as it does for 4,4'-diethoxyazoxybenzene (68), then quartic terms will have to be retained because such an effect cannot be accounted for simply in terms of the pseudo-potential for non-cylindrically symmetric molecules when this is restricted to quadratic terms. We shall not attempt calculations with the extended potential here because the available experimental evidence does not warrant such an extension.

CHAPTER FOUR

SPIN RELAXATION IN LIQUID CRYSTALS

4.1 Introduction

In this Chapter and in the following ones some static and dynamic aspects of liquid crystals are investigated using electron resonance spectroscopy. This technique can in fact often be used to investigate a diamagnetic system simply by adding a radical, or spin probe, whose interaction with its environment is reflected in the electron resonance spectrum. The nature of the system should, of course, play a dominant role in the choice of spin probe. For example if the system to be studied is a liquid crystal, or a membrane, then two properties of the spin probe are of prime importance. The molecules must deviate significantly from spherical symmetry so that they may be highly oriented by their anisotropic environment. Secondly there must be considerable anisotropy in the magnetic interactions in order for the extent of the partial alignment to be readily discernable in the electron resonance spectrum (38). These anisotropic interactions may also influence the widths of the lines as well as their positions because the anisotropy coupled to the molecular reorientation invariably constitutes a powerful spin relaxation process (38). Consequently the spectrum of the spin probe may often exhibit a characteristic linewidth variation and, because of the anisotropic nature of the environment, this variation will depend on the sample orientation with respect to the magnetic field. An understanding of such linewidth effects is

important not only as an aid to a correct spectral analysis but also because the linewidths contain valuable information relating to both the dynamic and static behaviour of the system (38). The static information obtainable includes the orientational order parameters, as $\bar{P}_2$ and $\bar{P}_4$. Their values and their temperature dependence provide a test for the statistical theories of the mesophase (c.f. the previous Chapters).

Several theories have been advanced to describe molecular reorientation in the presence of an ordering potential and they range from those in which the motion proceeds via small jumps (95-97) to the strong collision model where the jump angle can take any value (38,40,52).

In the next Chapters both these models will be used to interpret some experimental results and some pieces of theory necessary to connect the microscopic process to the observable spectrum will be developed. Our aim will be twofold. Firstly to obtain a qualitative description of the reorientation and try to distinguish between the models. Secondly to obtain values for the physically significant parameters of the models, such as the correlation times for reorientation of the long axis and about the long axis in the strong collision model, or the parallel and perpendicular components of the rotational diffusion tensor in the diffusion model. We shall treat in some detail the problems encountered in this type of analysis later on. In this Chapter we shall instead discuss some background material necessary for the successive developments.

4.2 Spin Relaxation Theory

This section gives a brief summary of the theory of spin relaxation originally due to Bloch (99), Redfield (100) etc..(101). To start with, it is useful to recall that the state of any system, classical or quantum, can be described in terms of an operator called the density operator or the density matrix of that system (102). In fact any observable $A(t)$ can be calculated from the density operator $\rho(t)$ at a given time t as (103)

$$A(t) = \text{Tr}\{\rho(t)A\}, \quad (4.1)$$

where $\text{Tr}\{\dots\}$ indicates an ordinary trace or an integral over the phase space as appropriate. The time evolution of ρ is governed by the Liouville equation

$$\begin{aligned} \dot{\rho}(t) &\equiv \frac{\partial}{\partial t} \rho(t) = -i [H, \rho(t)] \\ &= -iH^{\times} \rho(t). \end{aligned} \quad (4.2)$$

Here H is the hamiltonian of the system; the square brackets denote a commutator in the quantum case ($\hbar = 1$ is used here) and $\sqrt{-1} \equiv i$ times the Poisson brackets in the classical case. The operator $H^{\times}$ acts on operators producing their commutator with the hamiltonian. Operators acting on operators to give other operators are called superoperators and $H^{\times}$ is often called the Liouville superoperator. The algebra of superoperators is treated in detail elsewhere e.g. by Muus (104); here we just mention two properties which will be used later, firstly that the eigenvalues of $H^{\times}$ are energy differences (as directly observed in

spectroscopy) and secondly that

$$\exp(H) A \exp(-H) = \exp(H^X) A. \quad (4.3)$$

In a magnetic resonance experiment (105) the observable can be related to a component M_α of the complex magnetization at a certain frequency (or time). This in turn can be related to the expectation value of a particular spin operator S_α , where $\alpha=x,y,z$. As a simple example,

$$\begin{aligned} M_\alpha(t) &= g\beta \text{Tr}\{S_\alpha \rho(t)\} \\ &= g\beta \text{Tr}_S \{S_\alpha \sigma(t)\}. \end{aligned} \quad (4.4)$$

where g is the g factor and β the electron Bohr magneton. The last equation illustrates the obvious fact that to calculate spin properties we do not need the complete density matrix but just a spin density matrix σ ; this is obtained from the complete density matrix by summing over all degrees of freedom except the spin. Tr_S indicates the remaining trace over the spin variables. In the following we shall therefore only concern ourselves with the problem of finding an approximate expression for $\sigma(t)$. A natural starting point to do this is to divide the total system in two parts: a spin system and a bath. Neglecting intermolecular spin couplings, the spin system will be a single radical. The bath (or lattice) is weakly coupled to the spin system; it affects the spins and as we shall see later, causes their relaxation, but it is negligibly affected by the spins. Corresponding to this separation the

total hamiltonian is

$$H = H_0 + H_b + H_1,$$

where H_0 is the hamiltonian for the spin system in the presence of static magnetic field, H_b is the hamiltonian of the bath, dependent on position and orientation of the particles, H_1 is the (weak) coupling term. In accord with these definitions

$$H_0^\times H_b \equiv [H_0, H_b] = 0;$$

$$H_0^\times H_1 \equiv [H_0, H_1] \neq 0;$$

$$H_b^\times H_1 \equiv [H_b, H_1] \neq 0.$$

In the following, it should be remembered that we treat the bath as a classical system and the spins as a quantum one, even though a uniform notation is adopted. The Liouville equation for the total density matrix becomes

$$\dot{\rho} = -i(H_0^\times + H_b^\times + H_1^\times)\rho. \quad (4.5)$$

It is convenient to transform equation (4.5) to a new representation by writing e.g. $\rho = \exp\{i(H_0^\times + H_b^\times)t\}\rho^I$. Equation (4.5) then becomes

$$\dot{\rho}^I = -iH_1^{I\times} \rho^I.$$

This has the formal solution

$$\rho^I(t) = \exp\{-i \int_0^t dt' H_1^I(t')^\times\} \rho^I(0) \quad (4.6)$$

We now assume, as usual, that at time zero the spin system and the bath are not coupled (106,107) so that the total density is

$$\rho(0) = \rho_b \sigma(0) \quad \text{or} \quad \rho^I(0) = \rho_b^I \sigma^I(0), \quad (4.7)$$

where ρ_b is the equilibrium density of the bath i.e. its Boltzmann distribution. Substituting in equation (4.6) and remembering that the trace of a product of operators is independent on their representation we find

$$\overline{\sigma^+(t)} = \overline{\exp\{-i \int_0^t dt' H_1^+(t')^\times\} \sigma^+(0)}, \quad (4.8)$$

where we have introduced the definitions $\sigma^+ \equiv \exp(iH_0^\times t) \sigma$ and $H_1^+ \equiv \exp(iH_0^\times t) H_1$. This representation is often called the interaction representation. The upper bar indicates an average over the bath variables i.e. $\text{Tr}_b \{(\dots) \rho_b\}$ and in practice for our case this will mean an ensemble average over the orientations of the radical. We are now left with the problem of evaluating the right hand side of equation (4.8). To do this we shall follow Freed (108) and use Kubo's cumulant method (72). According to cumulant theory

$$\overline{\exp\{-i \int_0^t dt' H_1^+(t')^\times\}} = \exp K(t). \quad (4.9)$$

The cumulant function $K(t)$ is given by (108)

$$\begin{aligned}
 K(t) &= \sum_{n=1}^{\infty} \frac{1}{n!} \int_0^t dt_1 \dots \int_0^t dt_n \langle T H_1^+(t_1)^{\times} H^+(t_2)^{\times} H^+(t_2)^{\times} \dots H_1^+(t_n)^{\times} \rangle_C \\
 &= \sum_{n=1}^{\infty} \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \langle H_1^+(t_1)^{\times} \dots H_1^+(t_n)^{\times} \rangle_C
 \end{aligned} \quad (4.10)$$

where $\langle \dots \rangle_C$ is a cumulant average and T is a time ordering operator, which ensures that the time dependent operators on its right are arranged in chronological order. Substitution of equation (4.9) in equation (4.8) and differentiation gives the equation of motion

$$\dot{\sigma}^+(t) = \dot{K}(t) \sigma^+(t). \quad (4.11)$$

The terms in equation (4.10) vanish if any of the $H_1^+(t)^{\times}$ are uncorrelated, so that the only nonvanishing contributions come from times less than a characteristic correlation time τ . It is then reasonable to look for an approximate asymptotic solution $\dot{K}(t \rightarrow \infty)$ valid for $t \gg \tau$. If this condition is satisfied the upper limits in the time integration can be taken as infinity. Since we can define $H_0 = H_0 + \overline{H_1(t)}$ and $H_1(t) = H_1(t) - \overline{H_1(t)}$ we shall take $\overline{H_1(t)} = \overline{H_1^+(t)} = 0$ in the following. Using this fact and cumulant algebra it is not difficult to show that, to second order,

$$\dot{K}(\infty) = - \int_0^{\infty} dt' \overline{H_1^+(t)^{\times} H_1^+(t-t')^{\times}} \quad (4.13)$$

We shall retain only this term in the expansion, an approximation which is expected to be valid only if $|\overline{H_1(t)}|^2 \tau^2 \ll 1$ where τ is a

characteristic correlation time. Transforming back from the interaction representation we find

$$\hat{K}(\infty) = \exp(iH_0^x t)^x R, \quad (4.14)$$

where

$$R = - \int_0^\infty dt' H_1(t)^x \exp(iH_0^x t') H_1(t-t')^x. \quad (4.15)$$

The (super) matrix R defined in this way is just the celebrated Redfield matrix. It is easy to show that in a basis of eigenvectors of H_0 , where $H_0|a\rangle = E_a|a\rangle$, the matrix elements of R are explicitly

$$\begin{aligned} R_{aa'bb'} &= L_{abb'a'}(\omega_{ab}) + L_{abb'a'}(\omega_{b'a'}) - \delta_{a'b'} \sum_c L_{accb}(\omega_{cb}) \\ &- \delta_{ab} \sum_c L_{b'cca'}(\omega_{b'c}), \end{aligned} \quad (4.16)$$

where δ_{ab} is a Kronecker delta and

$$L_{abb'a'}(\omega) \equiv \int_0^\infty \overline{\langle a|H_1(t)|b\rangle \langle b'|H_1(t-t')|a'\rangle} \exp(-i\omega t') dt'. \quad (4.17)$$

The quantity $L_{abb'a'}(\omega_{ab})$ is then defined as the Fourier-Laplace transform at frequency $\omega_{ab} = (E_a - E_b)/\hbar$ of the dynamic hamiltonian correlation function. In practice the imaginary part of the transform can be neglected (109) and the Redfield matrix is just

$$\begin{aligned} R_{aa'bb'} &= 2J_{aba'b'}(\omega_{ab}) - \delta_{ab} \sum_c J_{acbc}(\omega_{cb}) \\ &- \delta_{ab} \sum_c J_{b'ca'c}(\omega_{b'c}). \end{aligned} \quad (4.18)$$

To derive equation (4.18) we have used the fact that H_1 is an Hermitian operator and introduced the usual notation

$$J_{aba'b'}(\omega) = \int_0^\infty \langle a | H_1(t) | b \rangle \langle a' | H_1(t-t') | b' \rangle e^{i\omega t} dt'. \quad (4.19)$$

The following relations are easily proved

$$J_{aba'b'}(\omega) = J_{b'a'ba}(\omega) = J_{aba'b'}(-\omega) = J_{bab'a'}(\omega)^* \quad (4.20)$$

If we now consider again the equation for the spin density matrix the following results are obtained immediately. In the interaction representation

$$\dot{\sigma}_{aa'}^+(t) = \sum_{bb'} \exp[i(\omega_{aa'} - \omega_{bb'})t] R_{aa'bb'} \sigma_{bb'}^+(t) \quad (4.21)$$

and in the ordinary representation

$$\dot{\sigma}_{aa'}(t) = -i\omega_{aa'} \sigma_{aa'}(t) + \sum_{bb'} R_{aa'bb'} \sigma_{bb'}(t). \quad (4.22)$$

In matrix form we have

$$\dot{\sigma} = (-iH_0^\times + R)\sigma. \quad (4.23)$$

If the relaxation term R is zero the solution is just an oscillation about σ_{eq} , if R is non zero the oscillation becomes damped, as we might expect. The real part of R is the damping term which relaxes the initially non-equilibrium situation. It is obvious from its physical

significance and also verifiable explicitly that R does not act on the equilibrium density matrix i.e. $R\sigma_{eq}=0$. We could then write also

$$\dot{\sigma} = -iH_0^x \sigma + R(\sigma - \sigma_{eq}), \quad (4.24)$$

as is sometimes found in the literature (110).

Equation (4.23) describes the evolution of the spin density matrix under the action of the bath. In an electron resonance experiment we are usually interested in measuring the complex magnetization in a plane perpendicular to the static magnetic field B_0 . A weak radio-frequency field perpendicular to B_0 is applied and the rate of change in the magnetization of the sample is monitored. To keep into account the interaction with the radiofrequency field B_1 we assume that, being weak, it produces only a linear response in the density matrix. We then have

$$\frac{\partial \sigma}{\partial t} = -i H_0^x \sigma + \left(\frac{\partial \sigma}{\partial t} \right)_{\text{relax.}} + \left(\frac{\partial \sigma}{\partial t} \right)_{\text{r.f.}} \quad (4.25)$$

$$= \{-iH_0^x + R -iH_{r,f}^x(t)\}\sigma, \quad (4.26)$$

where R is the relaxation matrix previously determined and $H_{r,f}$ is the perturbing Hamiltonian:

$$H_{r,f} = \omega_1 \{S_+ \exp(-i\omega t) + S_- \exp(i\omega t)\}, \quad (4.27)$$

$$\omega_1 = g\beta B_1/\hbar. \quad (4.28)$$

By Fourier transformation of equation 4.26 we find

$$\sigma(\omega) = \{ i\omega - R + iH_0^x \}^{-1} \{ -i\omega_1 S_+^x \sigma(2\omega) - i\omega_1 S_-^x \sigma(0) \} \quad (4.29)$$

where

$$\sigma(\omega) = \int_{-\infty}^{\infty} \sigma(t) \exp(-i\omega t) dt \quad (4.30)$$

and $\sigma(0)$ is the equilibrium spin density matrix. The non-resonant term $\omega_1 S_+^x \sigma(2\omega)$ on the right can usually be neglected and, if we assume $B_1 \ll B_0$ and $g\beta B_0 \ll kT$, the other term becomes (111)

$$-i\omega S_-^x \sigma(0) \approx -iCS_- , \quad (4.31)$$

where C is a real constant. For an unsaturated absorption experiment the line shape is (111-113)

$$\begin{aligned} S(\omega) &\propto \text{Im}\{\text{Tr}(S_x \sigma_{-1})\} = \text{Im} \sum_a \langle a | S_x | a-1 \rangle \langle a-1 | \sigma | a \rangle \\ &= \text{Im}\{S_+ \cdot \sigma\}, \end{aligned} \quad (4.32)$$

where S_+ is the $(2S+1)$ dimensional vector formed with the elements $\langle a | S_+ | b \rangle$. Substitution of the expression already found for $\sigma(\omega)$ gives

$$S(\omega) \propto -\text{Re} \{ \tilde{S}_- M(\omega)^{-1} S_- \} , \quad (4.33)$$

where we have defined $M \equiv -iH_0^x - i\omega + R \quad (4.34)$

$$M_{aa'bb'} = i(\omega_{a'a} - \omega) \delta_{ab} \delta_{a'b'} + R_{aa'bb'}. \quad (4.34)$$

In electrostatics the first derivative of $S(\omega)$ is usually measured. In the present formalism this is just

$$S'(\omega) = -\frac{1}{\pi} \text{Im} \left\{ \sum_a (S_{a-1,a})^2 / [i(\omega_{a'a} - \omega) + \Gamma_a] \right\}. \quad (4.35)$$

Let us now examine the spectrum in the limiting situation that the R matrix is diagonal. With this restriction S is diagonal as well and we can write

$$M_{a-1,a,b-1,b} = \{i(\omega_a - \omega) + \Gamma_a\} \delta_{ab}. \quad (4.36)$$

It follows that

$$\begin{aligned} S(\omega) &= \text{Re} \left\{ \sum_a (S_{a-1,a})^2 / [i(\omega_a - \omega) + \Gamma_a] \right\}, \\ &= \sum_a g_a L(\omega, \omega_a, \Gamma_a), \end{aligned} \quad (4.37)$$

where $g_a = (S+a)(S-a+1)$ and $L(\omega, \omega_a, \Gamma_a)$ is a lorentzian line shape i.e.

$$L(\omega, \omega_0, T_2^{-1}) = \frac{1}{\pi} \text{Re} \{ i(\omega - \omega_0) + T_2^{-1} \}^{-1}. \quad (4.38)$$

In our case

$$L(\omega, \omega_a, \Gamma_a) = -\text{Re} \{ 1 / [i(\omega_a + i\text{Im}\Gamma_a) - i\omega + \text{Re}\Gamma_a] \}. \quad (4.39)$$

Thus, when R is diagonal, the spectrum is a sum of lorentzians;

$(\text{Re}\Gamma_a) = \text{Re } R_{a-1,a,a-1,a}$ is a linewidth and $\text{Im}\Gamma_a$ is a (dynamic) frequency shift. A common more complex situation arises when a group of transitions is degenerate i.e. they have the same transition frequency ω_k but these are well separated from the others or, in other words, when the M matrix is block diagonal. The block corresponding to the degenerate set has to be inverted explicitly. Sometimes the inversion of the block can be done analytically (c.f. Chapter 7) but in general it is necessary to invert numerically the matrix for every frequency at which the spectrum has to be calculated. However, the situation, even in the general case of degenerate and non-degenerate transitions is not as complicated as it may seem. This is firstly because we are only interested in calculating certain elements of M^{-1} i.e. the $M_{a-1,a,b-1,b}^{-1}$. An inspection of the M matrix shows that it is possible to permute its rows and columns and rearrange all of these elements in a block matrix of dimension $2S \times 2S$, which is quite a dramatic reduction in size from the original space of dimensions $(2S+1)^2 \times (2S+1)^2$. For a triplet, as an example, the reduction is from a 9×9 matrix to a 2×2 . The contraction of the total Liouville space to the $2S$ dimensional "transition" space can be achieved because of certain restrictions on the subscripts of the relaxation matrix coming, physically, from energy conservation(100).

Summarizing, the Liouville space formalism offers a compact and general way of calculating the spectrum. In the fast motion limit the relaxation operator has been shown to coincide with the Redfield matrix. A contraction of the total Liouville space is possible reducing its

dimension to $2S$ i.e. to the number of allowed transitions. It is worth pointing out that the formalism does not depend on having degenerate or nondegenerate transitions as does the usual Redfield treatment. An expression is given for the total spectrum i.e. $S(\omega) \propto \text{Re}(S_+ M^{-1} S_-)$ and it just reduces to the proper limiting cases for degenerate and non-degenerate transitions. The method is particularly useful in problems like the one of the angular dependence of the electron resonance spectrum treated in this thesis since by changing the angle the transitions can pass from non-degenerate to degenerate and viceversa.

4.3 The Static Spin Hamiltonian

The calculation of the spectrum outlined in the previous Section requires the knowledge of the transition frequencies and of the relaxation matrix of the system under consideration. The calculation of the transition frequencies is treated here.

Consider the total time dependent spin hamiltonian $H(t)$, that is the unperturbed spin hamiltonian H_0 together with the spin-bath coupling hamiltonian H_1 . Since in the derivation of the Redfield matrix we have supposed that the dynamic hamiltonian has zero average, in the following we shall define $H \equiv \overline{H(t)}$ (static hamiltonian) and $H_1(t) \equiv H(t) - \overline{H(t)}$ (dynamic hamiltonian). We shall use the notation $\overline{H}$ instead of H_0 . The transition frequencies are then obtained from $\overline{H}$ and the elements of the relaxation matrix from the correlation function of $H_1(t)$. The total spin hamiltonian $H(t)$, since it contains the coupling between the spin system and the thermal bath, will depend both on spin and spatial variables. We shall find it convenient to write the hamiltonian $H(t)$ as a contraction of irreducible tensors, which at a certain instant of time is just,

$$H = \sum_{\mu} (-)^p F_{\mu}^{(L,p)} T_{\mu}^{(L,-p)}. \quad (4.40)$$

In this expression μ denotes the nature of the interaction, L its rank and F its strength, while T is the corresponding spin tensor. Since we shall assume that the molecular reorientation is the only relaxation mechanism for the spins, equation (4.40) gives also the hamiltonian at a given orientation. The choice of using irreducible tensors appears therefore as a very natural one, given their simple

transformation properties under rotation. The time dependence can be conveniently separated out by writing the tensors T in the molecular coordinate system in terms of the same tensors in a coordinate system fixed in the laboratory. It is convenient to choose the z axis of this laboratory system, which we call the d frame, along the director. The spin hamiltonian is then

$$H(t) = \sum_{\mu} (-)^P F_{\mu}^{(L,p)} D_{q,-p}^L(t) T_{\mu}^{(L,q)}. \quad (4.41)$$

Provided the molecular reorientation is fast on our experimental time scale, the static spin hamiltonian can be obtained from equation (4.41) by taking an ensemble average over the orientations.

$$\bar{H} = \sum_{\mu} (-)^P F_{\mu}^{(L,p)} \overline{D_{q,-p}^L} T_{\mu}^{(L,q)}. \quad (4.42)$$

The symmetry of the mesophase can now be employed to restrict the number of non-vanishing order parameters. If the mesophase is uniaxial, then

$$\overline{D_{q,-p}^L} = \overline{D_{0,-p}^L} \delta_{0p},$$

and

$$\bar{H} = \sum_{\mu} (-)^P F_{\mu}^{(L,p)} \overline{D_{0,-p}^L} T_{\mu}^{(L,0)}. \quad (4.43)$$

If the director is not parallel to the stationary magnetic field we require one more transformation to express the spin operators in terms of their components in a frame with the z axis along the magnetic field

(the B frame). The result is

$$H(t) = \sum (-)^P F_{\mu}^{(L,P)} D_{q,-p}^L(t) D_{r,q}^L T_{\mu}^{(L,r)} \quad (4.44)$$

and

$$\bar{H} = \sum (-)^P F_{\mu}^{(L,P)} \overline{D_{0,-p}^L} D_{r,0}^L T_{\mu}^{(L,r)}. \quad (4.45)$$

For all the practical cases only the angle γ between the z axes of the B frame and the d frame needs to be specified, so only the rotation $D_{r,q}^L(0\gamma 0)$ needs to be considered.

The static spin hamiltonian in equation (4.45) determines of course the line positions in the spectrum. It can be rewritten formally as the static hamiltonian for a cylindrically symmetric species i.e.

$$\bar{H} = \sum \tilde{F}_{\mu}^{(L,0)} D_{r,0}^L T_{\mu}^{(L,r)}, \quad (4.46)$$

where

$$\tilde{F}_{\mu}^{(L,0)} = \sum (-)^P F_{\mu}^{(L,P)} \overline{D_{0,-p}^L}, \quad (4.47)$$

is called a partially averaged tensor (38). This useful result shows that, irrespective of the symmetry of the probe, the line positions are formally that of a pseudomolecule with the symmetry of the mesophase (c.f. Chapter 1). The spectrum of a probe dissolved in a liquid crystal can therefore be quite different from that in the isotropic phase. In fact, taking the isotropic limit of equation (4.46) i.e. letting

the order parameter go to zero, we see that

$$\overline{H} = \sum_{\mu} F_{\mu}^{(0,0)} T_{\mu}^{(0,0)}. \quad (4.48)$$

In other words, in an isotropic solvent the anisotropy in the magnetic interactions is completely averaged to zero, in the fast motion limit that we have assumed so far. As a trivial consequence the spectrum is angular independent (isotropic). By contrast, in an ordered mesophase non-scalar interactions can survive even in the fast motion limit and the spectrum of an oriented probe shows a dramatic change from the isotropic one. The number of lines, their position, their shape can change; furthermore the spectrum can exhibit variations when the angle between field and director is changed. As far as the line positions are concerned, it is not necessary to go into details of these changes: having reduced the static hamiltonian to that of a cylindrically symmetric pseudomolecule, these details can be found in many textbooks (114,115). We shall just report the results for the important case of a spin probe containing one unpaired electron which interacts with a single magnetic nucleus of spin I. The observed resonant fields are, to first order in $|a/\omega_0|$,

$$B_r = B_0 - \bar{a}(\gamma) \hbar m / \{\bar{g}(\gamma) \beta\}, \quad (4.49)$$

$$B_0 = \hbar \omega_0 / \{\bar{g}(\gamma) \beta\}, \quad (4.50)$$

where ω_0 is the operating frequency of the spectrometer, and neglecting any nuclear quadrupole interaction. The electron

resonance spectrum contains $(2I+1)$ hyperfine lines. The angular dependent coupling constant and g factor are

$$\bar{g}(\gamma) = \{g^2 + (g_{\parallel}^2 - g_{\perp}^2) \cos^2 \gamma\}^{\frac{1}{2}} \quad (4.51)$$

and

$$\bar{a}(\gamma) = \{g_{\perp}^2 \bar{A}_{\perp}^2 + (g_{\parallel}^2 \bar{A}_{\parallel}^2 - g_{\perp}^2 \bar{A}_{\perp}^2) \cos^2 \gamma\}^{\frac{1}{2}} / \bar{g}(\gamma). \quad (4.52)$$

The partially averaged components of the hyperfine tensor A are defined as

$$\bar{A}_{\parallel} = a + (2/3)^{\frac{1}{2}} \sum_p (-)^p A^{(2,p)} \overline{D_{0,-p}^2}, \quad (4.53)$$

$$\bar{A}_{\perp} = a - (1/6)^{\frac{1}{2}} \sum_p (-)^p A^{(2,p)} \overline{D_{0,-p}^2}, \quad (4.54)$$

where a is the scalar coupling constant.

4.4 The Dynamic Spin Hamiltonian

The general form for the dynamic hamiltonian $H_1(t)$, in the laboratory frame, is obtained by subtracting equation (4.44) and equation (4.45), as

$$H_1(t) = \sum (-)^P F_{\mu}^{(L,p)} D_{-r,q}^L \{ D_{q,-p}^L(t) - \overline{D_{0,-p}^L} \delta_{0q} \} T_{\mu}^{(L-r)}, \quad (4.55)$$

$$= \sum (-)^r F_{\mu}^{L,r}(t) T_{\mu}^{L-r}. \quad (4.56)$$

We have defined

$$F_{\mu}^{(L,r)} = \sum (-)^{p+r} F_{\mu}^{(L,p)} \{ D_{q,-p}^L(t) - \overline{D_{0,-p}^L} \delta_{0q} \} D_{-r,q}^L. \quad (4.57)$$

The spectral densities to be calculated are

$$J_{aba'b'}(\omega) = \int_0^{\infty} \overline{\langle a | H_1(t) | b \rangle \langle a' | H_1(t+t') | b' \rangle} \cos \omega t' dt'. \quad (4.58)$$

Substituting equation (4.56) we find

$$J_{aba'b'} = \sum (-)^{r+r'} \langle a | T^{(L-r)} | b \rangle \langle a' | T^{(L'-r')} | b' \rangle J_{rr'}^{\mu\mu'}(\omega), \quad (4.59)$$

where

$$J_{rr'}^{\mu\mu'}(\omega) = \int_0^{\infty} \overline{F_{\mu}^{(L,r)}(t) F_{\mu'}^{(L',r')}(t+t')} \cos \omega t' dt'. \quad (4.60)$$

The problem of evaluating the Redfield matrix elements separates therefore in a spin part consisting in the calculation of certain matrix elements and in a properly dynamic part i.e. the calculation

of correlation function transforms $J_{rr'}^{\mu\mu'}$. The spin part can be dealt with quite simply by using angular momentum techniques. In practice the calculation of the spin part is the same as for isotropic systems provided the eigenstates of $\bar{H}$ are still the same. Therefore quite often the results for the spin part of the problems can be found in the standard works on spin relaxation in isotropic systems (109,116). We just mention here some well known results for a probe with a single electronic spin interacting with a nucleus of spin I . This includes the case of the popular nitroxide spin probes whose spectra we shall study in the next Chapters. As mentioned before, the calculation of the matrix elements of the Redfield matrix ought normally to be performed in a basis of eigenvectors of the static spin hamiltonian $\bar{H}$. It is convenient however to invoke the so called high-field approximation which corresponds to retaining only that part of the static hamiltonian which commutes with S_z and to work in the simple product basis $|S, m_S\rangle |I, m_I\rangle$ (see however Chapter 6). When the correlation times for the reorientation of the probe is greater than the inverse of the resonant frequency the terms which do not commute with S_z (i.e. the non-secular terms) can be neglected also in the dynamic spin hamiltonian. In this case the linewidth of the transition labelled by $m_I = m$ is just the inverse of a Redfield matrix element and can be written simply as (116)

$$T_2^{-1}(m) = A + Bm + Cm^2 \quad (4.61)$$

where

$$A = (2\omega_0^2 / 3g^2) J_0^{gg} + \{I(I+1)/4\} J_1^{AA} \quad (4.62)$$

$$B = (4\omega_0/3g) J_0^{gA} \quad (4.63)$$

$$C = (2/3) J_0^{AA} - (1/4) J_1^{AA} \quad (4.64)$$

To obtain these expressions only contributions from the hyperfine A tensor and from the g tensor have been considered. A simplified notation for the spectral densities ,e.g., J_0^{AA} instead of $J_0^{AA}(0)$ is adopted.

4.4 (b) The Correlation Function

In the previous sections we have shown that in the so called fast motion limit, i.e. when the bath relax much more quickly than the spin system, the linewidths and in general the shape of the spectrum depends on the spectral densities $J_{rr'}^{\mu\mu'}$. From equations (4.60) and (4.57) it is easy to see that the only dynamical quantity to be considered is the correlation function of the Wigner rotation matrices, that we write in general, for a stationary random process, as

$$\begin{aligned} \phi_{qpq'p'}^{LL'}(t) &= \overline{(D_{q,p}^L(0) - D_{q,p}^L) (D_{q',p'}^{L'}(t) - D_{q',p'}^{L'})^*} \\ &= \overline{D_{q,p}^L(0) D_{q',p'}^{L'}(t)^*} - \overline{D_{q,p}^L} \overline{D_{q',p'}^{L'}}, \end{aligned} \quad (4.65)$$

In practise we shall only need here correlation functions with $L=L'=2$ so the superscripts L, L' will be left implied. It is possible to restrict the number of subscripts in $\phi_{qpq'p'}$ by employing the symmetry of the mesophase and that of the probe (c.f. Chapter 5). As an example,

for a cylindrically symmetric probe and mesophase, the only case treated in this thesis,

$$\begin{aligned}\phi_{qpq'p'}(t) &= \phi_{qpqp} \delta_{qq'} \delta_{pp'} \\ &\equiv \phi_{qp}(t)\end{aligned}\tag{4.66}$$

The calculation of the correlation function requires some knowledge of the microscopic dynamic reorientation process. We assume it is a stochastic, Markov process (117), so that

$$\overline{D_{q,p}^L(0) D_{q,p}^{L*}(t)} = \int d\Omega_0 P(\Omega_0) D_{q,p}^L(\Omega_0) \int d\Omega P(\Omega_0|\Omega t) D_{q,p}^L(\Omega)^* \tag{4.67}$$

where $P(\Omega_0)$ is the equilibrium orientational distribution function and $P(\Omega_0|\Omega t)$ is the probability that, if the molecular orientation is Ω_0 at time zero, it will be Ω at time t ; it is called the conditional probability.

The equilibrium probability is given by

$$P(\Omega) = \exp\{-U(\Omega)/kT\} / \int \exp\{-U(\Omega)/kT\}, \tag{4.68}$$

where $U(\Omega)$ is the pseudo potential for the probe molecule.

According to a molecular field model of binary mixtures of rod-like particles (118) the pseudopotential for a solvent and solute molecule is

$$U^{(1)}(\cos\beta) = \sum_L \{ (1-x) u_L^{(11)} \bar{P}_L^{(1)} + x u_L^{(12)} \bar{P}_L^{(2)} \} P_L(\cos\beta), \tag{4.69}$$

(even)

$$U^{(2)}(\cos\beta) = \sum_{\substack{L \\ (\text{even})}} \{ (1-x) u_L^{(12)} P_L^{(1)} + x u_L^{(22)} P_L^{(2)} \} P_L(\cos\beta), \quad (4.70)$$

where the labels (1) and (2) indicate the solvent and the solute, x is the mole fraction of solute, the coefficients $u_L^{(ij)}$ are interaction parameters between molecules of species i and j . In electron resonance the solute (probe) concentration is vanishingly small. Taking the limit for $x \rightarrow 0$ of equations (4.69), (4.70) one finds (119,120)

$$\begin{aligned} U^{(1)}(\cos\beta) &= \sum_{\substack{L \\ (\text{even})}} u_L^{(11)} \bar{P}_L^{(1)} P_L(\cos\beta) \\ &\equiv kT \sum_L \lambda_L^{(1)} P_L(\cos\beta) \end{aligned} \quad (4.71)$$

$$\begin{aligned} U^{(2)}(\cos\beta) &= \sum_{\substack{L \\ (\text{even})}} u_L^{(12)} \bar{P}_L^{(1)} P_L(\cos\beta) \\ &\equiv kT \sum_{\substack{L \\ (\text{even})}} \lambda_L^{(12)} P_L(\cos\beta) \end{aligned} \quad (4.72)$$

Thus, when the probe concentration is very low, the two simultaneous equations (4.69), (4.70) become decoupled. The solute pseudopotential $U^{(2)}$ depends on the solvent-solute interaction $u_L^{(12)}$ and on the solvent order parameters $\bar{P}_L^{(1)}$; the solvent pseudopotential is the same as that of the pure mesophase. The quantities directly measurable in electron resonance are the solute order parameters $\bar{P}_L^{(2)}$ ($L=2,4$). They can be used, if the solvent order parameters are known, to extract some information on the solute-solvent interaction (118). By choosing the probe

to be as similar as possible to a nematogen, in the sense that

$u_L^{(12)} \sim u_L^{(11)}$ some insight can be gained on the mesophase itself (83).

From a more formal point of view, notice that the solute pseudopotential in equation (4.72) has the same angular dependence as the solvent one.

In particular by truncating the series at the first term ($L=2$) the Maier-Saupe like potential studied in Section 2.3 is recovered.

In this and the next Chapters the superscripts labelling solute and solvent will be omitted unless confusion can arise.

Let us now turn to the calculation of the conditional probability $P(\Omega_0|\Omega t)$. It is known that the conditional probability for a Markov process obeys an integral master equation and that under certain conditions (117) this can be reduced to a differential equation. We shall assume this to be the case and consider in brief two rather different limiting situations.

4.4 (c) The Strong Collision Model

The strong collision model (121,122) represents a process where the molecule of interest undergoes sudden changes in its orientation at time intervals τ . The time taken for the transition from one orientation to the other is supposed to be negligible; the orientational probabilities before and after the sudden change (collision) are assumed to be given by the equilibrium Boltzmann distribution. Under these conditions the rate of change of the conditional probability $P(\Omega_0|\Omega t)$ is simply

$$\frac{\partial}{\partial t} P(\Omega_0|\Omega t) = \frac{1}{\tau} \{P(\Omega) - P(\Omega_0|\Omega t)\}. \quad (4.73)$$

The general integral of this first order linear differential equation, subject to the initial condition $P(\Omega_0|\Omega_0) = \delta(\Omega_0 - \Omega)$ is

$$\begin{aligned} P(\Omega_0|\Omega t) &= \delta(\Omega - \Omega_0) \exp(-t/\tau) + P(\Omega) \{ 1 - \exp(-t/\tau) \} \\ &= P(\Omega) + \{ \delta(\Omega - \Omega_0) - P(\Omega) \} \exp(-t/\tau). \end{aligned} \quad (4.74)$$

This conditional probability obviously reduces to the equilibrium probability for very long times, as it has to be (117). Thus, in general, the quantity

$$\overline{D_{q,p}^L(0) D_{q,p}^{L*}(t)}$$

will reduce to $|D_{q,p}^L|^2$ at very long times and the correlation function $\phi_{q,p}(t)$ defined by equation(4.65) will then decay to zero. It is easy to calculate the correlation function $\phi_{q,p}$ at any instant of time t employing equation (4.74). The calculation shows that for a cylindrically symmetric probe and mesophase equation (4.66) is obeyed, and that

$$\phi_{q,p}(t) = \{ \overline{D_{q,p}^2 D_{q,p}^{2*}} - \bar{P}_2^2 \delta_{0q} \delta_{0p} \} \exp(-t/\tau). \quad (4.75)$$

Although this function has been employed to study the electron resonance spectrum of vanadyl chelates dissolved in a nematic mesophase (40), the use of a single correlation time ignores the anisotropic nature of the solute. This deficiency has been removed by assuming (52) that the correlation time depends on p but not q and so

$$\phi_{q,p}(t) = \{ D_{q,p}^2 D_{q,p}^{2*} - \bar{P}_2^2 \delta_{0q} \delta_{0p} \} \exp(-t/\tau_p). \quad (4.76)$$

In linewidth theory (c.f. the previous section) the second subscript of $\phi_{q,p}$ turns out to indicate the component of a certain (2nd rank) tensorial interaction so that this generalized strong collision model allows each component to decay with its own correlation time τ_p . Another form of equation (4.76) can be obtained by coupling the two Wigner rotation matrices as (34)

$$\begin{aligned} D_{q,p}^2 D_{q,p}^{2*} &= (-)^q {}^{-p} D_{q,p}^2 D_{-q,-p}^2 \\ &= (-)^q {}^{-p} \sum_L C(22L; q-q) C(22L; p-p) D_{0,0}^L. \end{aligned} \quad (4.77)$$

This gives

$$\phi_{q,p}(t) = (-)^q {}^{-p} \sum_{\substack{L \\ \text{(even)}}} \{ C(22L; q-q) C(22L; p-p) \bar{P}_L {}^{-\bar{P}}_L^2 \delta_{L2} \delta_{0q} \delta_{0p} \} \exp(-t/\tau_p) \quad (4.78)$$

For linewidth studies it is often useful to have the zero frequency Fourier transforms of $\phi_{q,p}(t)$, i.e. the spectral densities $j_{qp}(0)$. They are just

$$j_{qp}(0) = (-)^q {}^{-p} \sum_{\substack{L \\ \text{(even)}}} \{ C(22L; q-q) C(22L; p-p) \bar{P}_L {}^{-\bar{P}}_L^2 \delta_{L2} \delta_{0q} \delta_{0p} \} \tau_p. \quad (4.79)$$

After evaluation of the Clebsch-Gordan coefficients we find the explicit

expressions listed in Table 4.1.

TABLE 4.1 The spectral densities j_{qp} for the strong collision model

q	p	Spectral density $j_{qp}(0)$
0	0	$\{\frac{1}{5} + \frac{2}{7} \bar{P}_2 + \frac{18}{35} \bar{P}_4 - \bar{P}_2^2\} \tau_0$
± 1	0	$\{\frac{1}{5} + \frac{1}{7} \bar{P}_2 - \frac{12}{35} \bar{P}_4\} \tau_0$
± 2	0	$\{\frac{1}{5} - \frac{2}{7} \bar{P}_2 + \frac{3}{35} \bar{P}_4\} \tau_0$
0	± 2	$\{\frac{1}{5} - \frac{2}{7} \bar{P}_2 + \frac{3}{35} \bar{P}_4\} \tau_2$
± 1	± 2	$\{\frac{1}{5} - \frac{1}{7} \bar{P}_2 - \frac{2}{35} \bar{P}_4\} \tau_2$
± 2	± 2	$\{\frac{1}{5} + \frac{2}{7} \bar{P}_2 + \frac{1}{70} \bar{P}_4\} \tau_2$

Notice that the following symmetry relations are obeyed:

$$j_{qp} = j_{q,-p} = j_{-q,p} = j_{-q,-p} . \quad (4.80)$$

4.4 (d) The Diffusion Model

The equation of motion for the conditional probability for a particle undergoing a rotational Brownian motion subjected to a potential $U(\Omega)$ is, in coordinate free form (123),

$$-\frac{\partial}{\partial t} P(\Omega_0|\Omega t) = \Gamma P(\Omega_0|\Omega t) \quad (4.81)$$

$$= -J\left\{D J \frac{U}{kT}\right\} P(\Omega_0|\Omega t) - J D J P(\Omega_0|\Omega t).$$

This is subjected to the initial boundary condition

$$P(\Omega_0|\Omega_0) = \delta(\Omega - \Omega_0). \quad (4.82)$$

In equation (4.81) Γ is called the stochastic operator, J is an angular momentum operator in a particle fixed frame and in dimensionless form and finally D is the rotational diffusion tensor of the particle. The single particle potential U is a function of the molecular orientation. When U is a constant, equation (4.81) reduces to the well known equation of rotational diffusion in a isotropic medium; the eigenvalues and eigenfunctions of the stochastic operator are in that case (124)

$$E_{Jp} = D_1 \{J(J+1) + (D_{11}/D_1 - 1)p^2\}, \quad (4.83)$$

and
$$\psi_{Jqp}(\Omega) = \left(\frac{2J+1}{8\pi^2}\right)^{\frac{1}{2}} D_{q,p}^{J*}(\Omega), \quad (4.84)$$

if the diffusion tensor is cylindrically symmetric, as we shall assume from now on. The presence of the term containing the potential in

equation (4.81) causes in general Γ to be non hermitian. However, it can be shown that, if the detailed balance principle holds, Γ can be made hermitian by the transformation

$$\hat{\Gamma} = P^{-\frac{1}{2}} \Gamma P^{\frac{1}{2}} \quad (4.85)$$

where P is the equilibrium orientational distribution function and $\hat{\Gamma}$ is the hermitian stochastic operator. The existence of this transformation guarantees that Γ can be diagonalized and that its eigenvalues are real. The eigenvalues of Γ constitute a non-negative sequence; the reciprocal of the eigenvalues are the relaxation times of the process. The first eigenvalue of $\hat{\Gamma}$ is always zero, corresponding to the equilibrium probability which, being unaffected by the stochastic operator, has an infinite relaxation time. We shall employ the symmetrized version of the diffusion equation (98) in Chapter 5; by now we shall instead examine briefly the unsymmetrized problem, originally solved by Nordio and his group (96). They express Γ in Euler angles, where it has the form

$$\Gamma P(\Omega_0|\Omega t) = \nabla_{\Omega}^2 P(\Omega_0|\Omega t) + \frac{(\sin\beta)^{-1}}{kT} \frac{\partial}{\partial\beta} \{ \sin\beta \cdot P(\Omega_0|\Omega t) \frac{dU}{d\beta} \} , \quad (4.86)$$

where ∇_{Ω}^2 is the Laplacian in terms of the Euler angles $(\alpha\beta\gamma)$ describing the orientation of the molecule with respect to the director. The operator Γ is then given a representation in a Wigner rotation matrices basis (i.e., as we have seen, the eigenfunctions of $J D J = \nabla_{\Omega}^2$). For a cylindrically symmetric probe reorienting in a uniaxial mesophase it is clear that the angular momentum projection quantum numbers q

and p are still good labels for the eigenvalues of Γ . In other words the total representation of Γ factorizes in diagonal blocks labelled by q and p . In Nordio's notation the (q,p) block is called $-D_1 R^{qp}$ and one has

$$D_1^{-1} \frac{d}{dt} C_J^{qp} = \sum_{J'} (R^{qp})_{JJ'} C_{J'}^{qp}, \quad (4.87)$$

where the vector C^{qp} is defined through the expansion

$$P(\Omega_0 | \Omega t) = \sum_J C_J^{qp}(t) D_{q,p}^J(\Omega). \quad (4.88)$$

The explicit expression for the R^{qp} matrix is (96)

$$(R^{qp})_{JJ'} = -[J(J+1) + (D_{11}/D_1 - 1)p^2] \delta_{JJ'}, \quad (4.89)$$

$$-\frac{1}{2} \sum_L \lambda_L [J(J+1) - J'(J'+1) + L(L+1)] C(LJ'J; 0q)$$

$$\times C(LJ'J; 0p).$$

The parameters λ_L are the expansion coefficients for the orientational potential of a molecule,

$$U(\beta) = kT \sum_{\substack{L \\ \text{(even)}}} \lambda_L P_L(\cos\beta). \quad (4.90)$$

The axis of symmetry of the diffusion and of the ordering tensors are assumed to coincide. It has been shown by Nordio et al (96) that the solution to equation (4.87) subject to the initial condition

equation (4.82) is

$$P(\Omega_0|\Omega t) = \sum (2I+1) (X^{qp})_{JK} (X^{qp})_{KI}^{-1} \exp(D_1 r_K^{qp} t) D_{q,p}^{I*}(\Omega_0) D_{q,p}^J(\Omega), \quad (4.91)$$

where X is the transformation that diagonalizes R :

$$X^{-1} R X = r. \quad (4.92)$$

A lower case notation is introduced for the diagonal eigenvalues matrix. The zero frequency spectral densities calculated with this conditional probability can be written as (96)

$$j_{qp} \equiv j_{qp}(0) = \sum_{J=0} \left\{ \overline{D_{q,p}^2} \overline{D_{q,p}^{J*}} - \delta_{q0} \delta_{p0} \overline{D_{0,0}^2} \overline{D_{0,0}^J} \right\} \tau_{Jqp}, \quad (4.93)$$

where τ_{Jqp} are time constants defined by

$$\tau_{Jqp} = \frac{2J+1}{5 D_1} (R^{qp})_{2J}^{-1}. \quad (4.94)$$

The spectral densities obtained from this model obey certain symmetry rules because of the properties of the Clebsch-Gordan coefficients, in fact (96)

$$j_{q,p} = j_{-q,-p} = j_{q,-p} = j_{-q,p}. \quad (4.95)$$

4.4 (e) Computational Problems

The calculation of the spectral densities j_{qp} can be performed by inverting the matrix R^{qp} in equation (4.89) to determine the time constants τ_{Jqp} and then substituting in equation (4.93). The dimension of R corresponds to the numbers of terms retained in the series expansion (4.88) and is chosen to ensure convergence. A typical value is 30. The inversion of R has to be repeated for every (q,p) , for any D_{11}/D_1 and, of course for any order parameter $\bar{P}_2$ one is interested in. Computation time requirements can then be quite heavy for a complete set of calculations. Hemminga (128,129) quotes about 4 hours on a CDC CYBER 74.16 computer. Here we shall investigate how to reduce dramatically this time while getting a better insight into the theory. As a starting point we decompose R in three parts.

$$R = a + d + \lambda B, \quad (4.96)$$

where the matrices a , d , B are defined as

$$a_{JJ'} = -J(J+1) \delta_{JJ'}, \quad (4.97)$$

$$d_{JJ'} = - \left(\frac{D_{11}}{D_1} - 1 \right) p^2 \delta_{JJ'}, \quad (4.98)$$

$$B_{JJ'} = - \frac{1}{2} \{ J(J+1) - J'(J'+1) + 6 \} C(2J'J; 0q) C(2J'j; 0p). \quad (4.99)$$

We use a lower case notation for diagonal matrices. We assume, for the sake of simplicity, that the pseudopotential is of the Maier-Saupe type $U(x) = kT\lambda P_2(x)$. The following arguments can be generalized to

more complex potentials.

Suppose now we want to change the diffusion tensor. If $p=0$ (i.e. if we calculate j_{q0}) there is no dependence on $D_{||}/D_{\perp}$ and then no problem. If $p \neq 0$, notice that d_{JJ} is a multiple of the identity matrix and that it is the only part of R that contains $D_{||}/D_{\perp}$. We can write the matrix R as

$$R = (a + \lambda B) + d \quad (4.100)$$

$$\equiv C + d.$$

Now, if Q is the matrix that diagonalizes C ,

$$CQ = Qc, \quad (4.101)$$

then

$$\begin{aligned} Q^{-1} R Q &= c + Q^{-1} d Q \\ &= c + d, \end{aligned} \quad (4.102)$$

since d commutes with Q . Therefore the inverse of R is

$$R^{-1} = Q(c+d)^{-1} Q^{-1} \quad (4.103)$$

so that

$$\tau_{Jqp} = - \frac{2J+1}{5} \sum_K \frac{Q_{2K} Q_{KJ}^{-1}}{c_K - \left(\frac{D_{||}}{D_{\perp}} - 1\right) p^2}, \quad (4.104)$$

in units of $D_{\perp}^{-1}$. It is then not necessary to repeat the calculation of R^{-1} for every $D_{||}/D_{\perp}$: we just have to diagonalize the matrix C and invert its eigenvectors matrix Q once. Let us now return to the spectral densities j_{qp} . Substituting equation (4.104) in (4.93) and exchanging

the order of the summations on K and J we find

$$j_{qp} = - \sum_K \frac{Z_K^{qp}}{c_K - \left(\frac{D_{||}}{D_{\perp}} - 1 \right) p^2} \quad (4.105)$$

where the array Z^{qp} is

$$\begin{aligned} Z_K^{qp} = & \frac{(-1)^{q+p}}{5} Q_{2K} \\ & \times \sum_{J=0} (2J+1) \left\{ \sum_{\substack{J' \\ \text{(even)}}} C(2J', q-q) C(2JJ', p-p) \bar{P}_J \right. \\ & \left. - \bar{P}_2 \bar{P}_J \delta_{0q} \delta_{0p} \right\} Q_{KJ}^{-1} \end{aligned} \quad (4.106)$$

Equation (4.105) shows very clearly how the ratio $D_{||}/D_{\perp}$ affects the spectral densities. It allows a very efficient computation of the spectral densities and then of the linewidth coefficients in the case when the order parameter is kept constant while $D_{||}/D_{\perp}$ is changed, which is what is often required in practice. For example, the order parameter $\bar{P}_2$ can be determined from the line positions assuming a Maier-Saupe potential the interaction parameter λ can be determined e.g. from figure 2.1 (notice there $\xi = \frac{3}{2} \lambda$ is used) and the array Z^{qp} is calculated once and for all. The diffusion tensor components ratio $D_{||}/D_{\perp}$ is then determined by changing it until the linewidth coefficients agree with experiment. A slightly more complicated problem arises when we want to change the order parameter $\bar{P}_2$. This is because neither matrix B nor matrix a are a multiple of the identity so that the

commutativity assumed in equation (4.102) is not guaranteed. We can overcome the problem operating some transformations on the matrix R i.e.

$$\begin{aligned} (a+d)^{-\frac{1}{2}} R(a+d)^{-\frac{1}{2}} &= 1 + \lambda (a+d)^{-\frac{1}{2}} B(a+d)^{-\frac{1}{2}} \\ &\equiv 1 + \lambda G . \end{aligned} \quad (4.107)$$

Now, if S is the transformation that diagonalizes G, i.e. $GS=Sg$, then after some manipulations

$$R^{-1} = (a+d)^{-\frac{1}{2}} S(1+\lambda g)^{-1} S^{-1}(a+d)^{-\frac{1}{2}}, \quad (4.108)$$

and, in units of D_1^{-1} ,

$$\tau_{Jqp} = - \frac{2J+1}{5} d_{22}^{-\frac{1}{2}} d_{JJ}^{-\frac{1}{2}} \sum_k \frac{S_{2k} S_{kJ}^{-1}}{(1 + \lambda g_{kk})}. \quad (4.109)$$

Therefore, to calculate the time constants τ_{Jqp} at various values of λ (and then of $\bar{P}_2$) we have just to set up the matrix G, diagonalize it and invert its eigenvector matrix once; then perform the summation in equation (4.109) for every λ of interest. Notice that the formalism described here is even more convenient when the symmetrized version (98) of relaxation theory is used for then the inverse of the eigenvector matrix is just its hermitian conjugate.

CHAPTER FIVE

ANGULAR DEPENDENT LINEWIDTHS

5.1 Introduction

The magnetic field present in the electron resonance spectrometer is usually employed to align the director in the mesophase. It is, however, possible to vary the angle between the field and the director by proper application of an additional constraint to counterbalance the orienting effect of the magnetic field. A number of techniques have been developed for this purpose. They include spinning the sample (130-132) and the application of an electric field (133-135). As the angle between director and magnetic field changes, both the positions and the widths of the spectral lines can vary (52-55). From an analysis of the angular dependent linewidths in terms of the strong collision and diffusion model some static and dynamic informations can be obtained. The development of such an analysis should be of value also for the interpretation of spectra of spin probes dissolved in biological membranes (128, 129, 136-141) in view of the similarity between these anisotropic system and a smectic mesophase.

In this Chapter we report a study of the angular dependence of the electron resonance spectrum of a spin probe dissolved in a smectic A mesophase. The spectra are analysed to obtain the angular variation of the linewidth coefficients and hence the angular linewidth coefficients. These angular coefficients may be interpreted by employing a theory of spin relaxation based on the strong collision

model for molecular reorientation. Such an analysis yields values for the correlation times for reorientation about the long and short axes of the spin probe as well as the magnitude of the solute order parameter $\bar{P}_4$. The possibility of interpreting the angular linewidth coefficients in terms of a theory based on the diffusion model for molecular reorientation is also explored. Relatively straightforward expressions for these coefficients can only be obtained from the diffusion model when the orientational order is high, as it is in a smectic phase. The analysis of the angular linewidth coefficients then provides values for the components of the diffusion tensor parallel and perpendicular to the long axis of the spin probe. The large anisotropy in the diffusion tensor may be indicative of the unhindered molecular motion about the long axis.

Both models of molecular reorientation in a highly ordered system appear to provide a satisfactory account of the observed angular linewidth coefficients.

5.2 Experimental

The mesogen employed in this investigation was 3-N-(4'-ethoxybenzilideneamino)-6-n-butylpyridine. This is reported to melt at about 29°C to form a smectic phase which passes to a nematic mesophase at 49°C; the isotropic fluid is subsequently formed at approximately 54°C (143). The spin probe, (3-spiro-[2'-N-oxyl-3',3'-dimethyloxazolidine]) 5 α -cholestane was synthesised from 5 α -cholestan-3-one using the standard route (144). The molecular structure of this spin probe is shown in figure 5.1 together with the principal coordinate system for the magnetic interaction tensors. The transition temperatures for the mesogen were depressed several degrees by the addition of the spin probe but this will not affect our analysis of the line-width coefficients. A monodomain sample of the smectic mesophase was prepared in the following way. The sample was first heated, within the cavity of a Varian E-3 spectrometer, until the nematic phase was formed and at this point the director, or preferred molecular orientation, is aligned parallel to the magnetic field of the spectrometer. The field was then set to its maximum value of 6.5 kG and the temperature lowered slowly until the smectic A phase was formed. The surface forces, which can inhibit the production of a monodomain sample, were reduced by coating the tube with plastic (142). The electron resonance spectrum of the sample at 28°C was then measured as a function of its orientation relative to that of the magnetic field. The spectra obtained for all orientations contained the three hyperfine lines expected for a monodomain sample doped with a nitroxide spin probe. In addition the angular dependence of the nitrogen hyperfine spacing shows that the director remains parallel to the magnetic field on passing from the nematic to the smectic phase and so shows this to be smectic A (142).

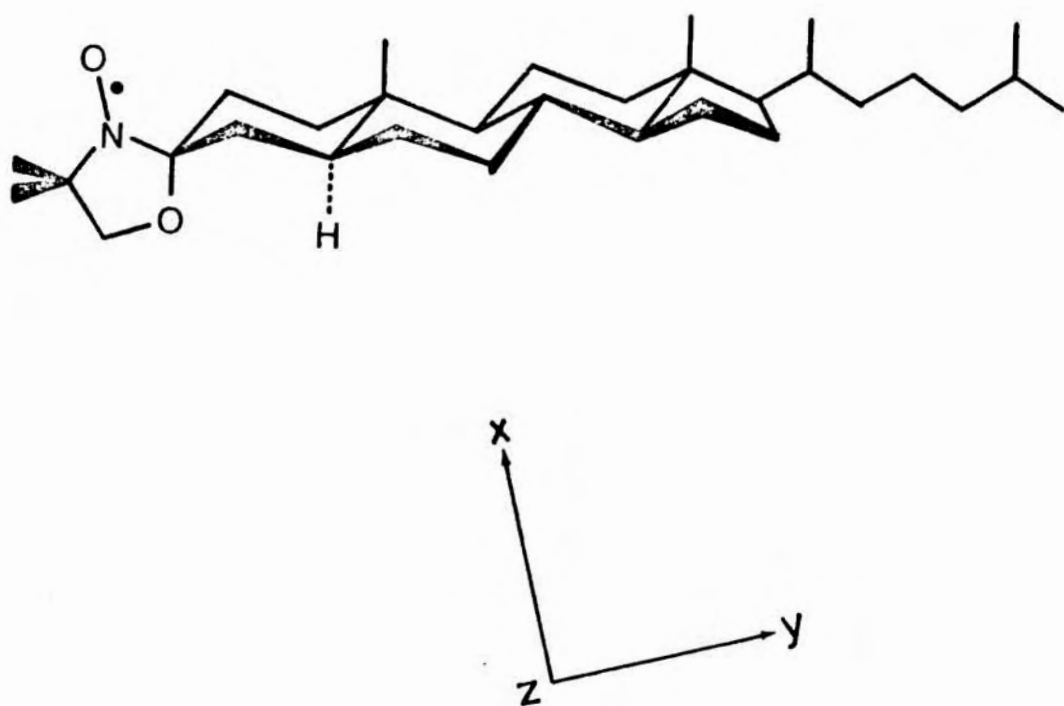


Figure 5.1 The structure of the spin probe and the principal coordinate system for the magnetic tensors.

The line shape is essentially gaussian because of inhomogeneous broadening caused by unresolved proton hyperfine structure. The linewidth was equated with the peak-to-peak separation. The widths of the three hyperfine lines were determined from that of the central line and the heights of the outer two lines relative to the central peak. These linewidths were then used to determine the linewidth coefficients in the expression

$$T_2^{-1}(m) = A + Bm + Cm^2, \quad (5.1)$$

where m is the nuclear quantum number. The observed angular dependence of these linewidth coefficients is shown in figure 5.2 and it is this dependence which we shall now examine in greater detail.

5.3 Angular Dependent Linewidths

The dominant relaxation process for a spin probe, similar to that employed in this study, is its molecular reorientation, with respect to the director, coupled to the anisotropy in the magnetic interactions. The observation of motional narrowed spectra from this system is important for it shows that the linewidths are directly related to the dynamic spin hamiltonian. In fact they are determined by the Fourier transform of the correlation function of the dynamic perturbation. For this problem the dynamic spin hamiltonian is conveniently written in irreducible tensor notation as (52):

$$H_1(t) = \sum_{\mu; p, q, r} (-1)^p F_{\mu}^{(2, p)} D_{r, q}^2 \{ D_{q, -p}^2(t) - D_{0, -p}^2 \delta_{0q} \} T_{\mu}^{(2, r)}. \quad (5.2)$$

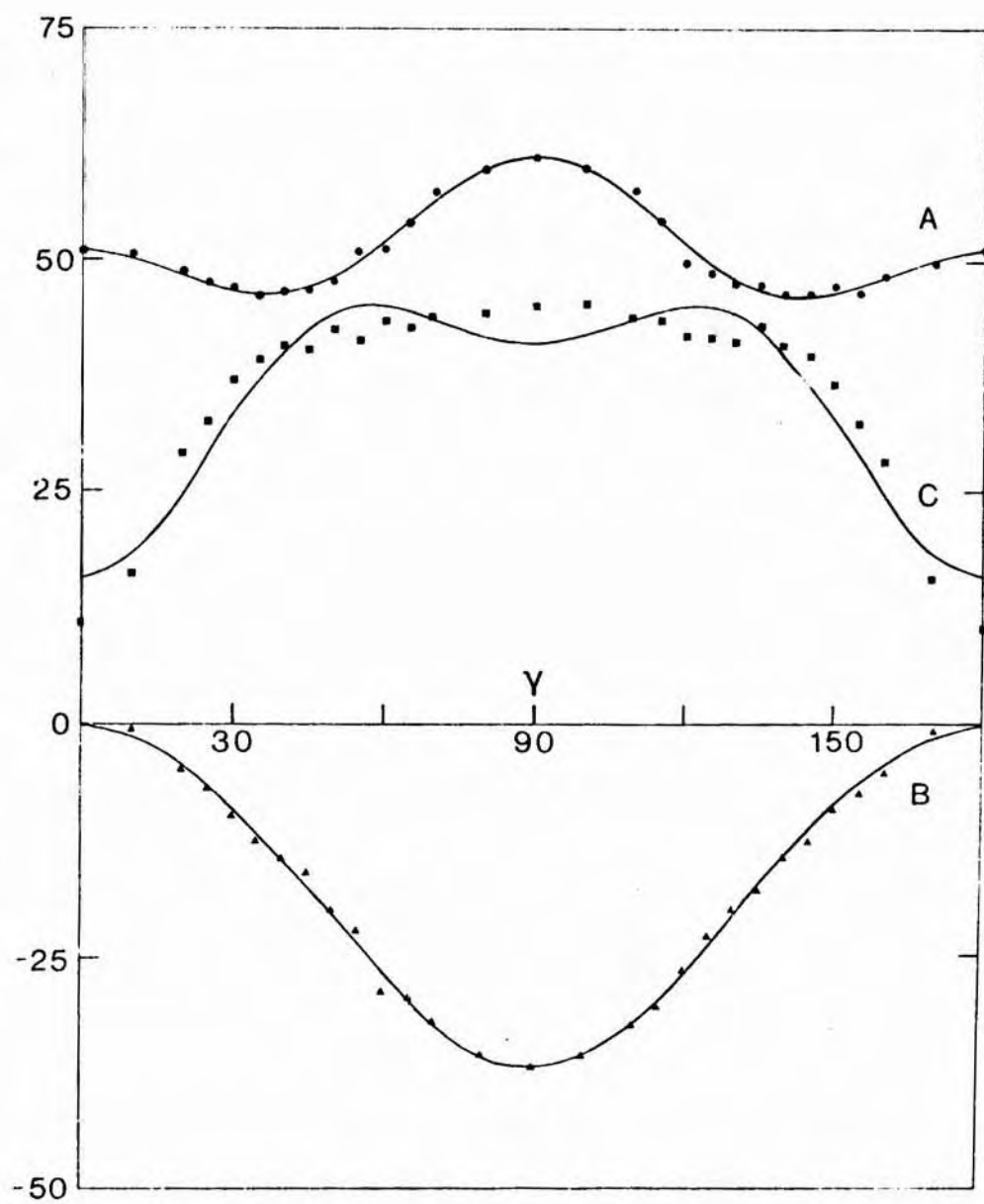


Figure 5.2 The angular dependence of the linewidth coefficients A($\bullet$), B($\blacktriangle$) and C($\blacksquare$); the linewidths are in Mrad.s^{-1} .

The time dependence in $H_1(t)$ is contained entirely in the Wigner rotation matrix $D_{q,-p}^2(t)$ relating the molecular coordinate system to a space fixed system containing the director. This space fixed coordinate system is connected to a second, which contains the magnetic field, by the rotation matrix $D_{r,q}^2$. The orientational order of the spin probe in the mesophase is given by the ensemble average of the third rotation matrix, $D_{0,-p}^2$. For douplet state species the only anisotropic magnetic interactions of any importance are the second rank Zeeman and hyperfine terms. The strength of these interactions is denoted by $F_\mu^{(2,p)}$ where the subscript μ indicates a particular term. Finally the relevant spin operators are represented by $T_\mu^{(2,r)}$. The dynamic aspects of the problem are contained therefore in the correlation function

$$\phi_{q,-p,-q',-p'}(t) = \overline{D_{q,-p}^2(0) D_{q',-p'}^{2*}(t) D_{0,-p}^2 D_{0,-p'}^{2*}} \delta_{0q} \delta_{0q'} \quad (5.3)$$

This may be simplified to

$$\phi_{q,-p}(t) = \overline{D_{q,-p}^2(0) D_{q,-p}^{2*}(t)} - \bar{P}_2^2 \delta_{0q} \delta_{0p} \delta_{qq'} \delta_{pp'} \quad (5.4)$$

by invoking the cylindrical symmetry of both the mesophase and the spin probe as we shall see later on. The complete cross correlation function $\psi_r^{(\mu\mu')}$ for the interactions μ and μ' is then

$$\psi_r^{(\mu\mu')}(t) = \sum_{\substack{L \\ \text{(even)} \\ p,q}} (-1)^{r-q} F_\mu^{(2,p)} F_{\mu'}^{(2,p)*} C(22L;r-r) C(22L;q-q) \phi_{q,-p}(t) P_L(\cos\gamma), \quad (5.5)$$

where $C(22L;r-r)$ is a Clebsch-Gordan coefficient (34). The restriction of the summation to even values of L results from the $D_{\infty h}$ symmetry of the smectic A phase and the properties of the Clebsch-Gordan coefficients require that the maximum value is four. The angular dependence of the correlation function is contained in the Legendre polynomial $P_L(\cos\gamma)$ where γ is the angle between the director and the magnetic field. Since the linewidths are proportional to the Fourier transform of $\psi(t)$ their angular dependence and hence that of the linewidth coefficients will be of the form (52)

$$A = A_0 + A_2 P_2(\cos\gamma) + A_4 P_4(\cos\gamma). \quad (5.6)$$

It is important to realise that this relatively simple angular dependence only obtains if the nuclear spin is quantised in the direction of the magnetic field (137). For the moment assume this to be the case. In general however, due to the effect of the pseudo-secular hyperfine terms in the hamiltonian, the direction of quantization of the nuclear spin will change as we change the angle between the director and the field. The effect that this has on the linewidths is examined in detail in the next Chapter.

The observed angular linewidth coefficients, listed in Table 5.1, were obtained by a least-squares fit of the angular dependence of the linewidth coefficients to the theoretical expression in equation (5.6). The theoretical angular dependence, calculated with these values, is plotted as the solid lines in Figure 5.2. The agreement between theory and experiment is seen to be extremely good for both the A and B

TABLE 5.1 The angular linewidth coefficients (Mrad.s^{-1})

Component L	A_L	B_L	C_L
0	52.7	-24.2	40.1
2	-10.3	24.6	-11.2
4	8.4	-0.6	-12.8

coefficients but not quite as impressive for C. The discrepancy might be attributed to imperfections in the monodomain sample as well as to the nuclear spin quantization effect and we shall return to this point later. In the following two Sections we shall see how these coefficients may be analysed using first the strong collision model and then the diffusion model.

5.4 The Strong Collision Model

As we saw in Section 4.4 (c) the 2nd rank Wigner rotation matrices correlation function may be written, for the generalized strong collision model, as

$$\phi_{q,-p}(t) = \{ \overline{D_{q,-p}^2} D_{q,-p}^{2*} - \bar{P}_2^2 \delta_{0q} \delta_{0p} \} \exp(-t/\tau_p) \quad (5.7)$$

The angular linewidth coefficients predicted by this relatively crude correlation function are (52)

$$A_0 = 2\omega_0^2 \{ g^{(2,0)^2} \tau_0(1-\bar{P}_2^2) + 2g^{(2,2)} \tau_2 \} / 15g^2 + I(I+1) \{ A^{(2,0)^2} \tau_0(1-\bar{P}_2^2) + 2A^{(2,2)^2} \tau_2 \} / 20, \quad (5.8)$$

$$A_2 = 4\omega_0^2 \bar{P}_2 \{ g^{(2,0)^2} \tau_0(1-\bar{P}_2^2) - 2g^{(2,2)^2} \tau_2 \} / 21g^2 + I(I+1)\bar{P}_2 \{ A^{(2,0)^2} \tau_0(1-\bar{P}_2^2) - 2A^{(2,2)^2} \tau_2 \} / 28, \quad (5.9)$$

$$A_4 = 4\omega_0^2 \{ 3g^{(2,0)^2} \tau_0(\bar{P}_4 - \bar{P}_2^2) + g^{(2,2)^2} \tau_2 \bar{P}_4 \} / 35g^2 - I(I+1) \{ 3A^{(2,0)^2} \tau_0(\bar{P}_4 - \bar{P}_2^2) + A^{(2,2)^2} \tau_2 \bar{P}_4 \} / 35, \quad (5.10)$$

$$B_0 = 4\omega_0 \{ g^{(2,0)} A^{(2,0)} \tau_0(1-\bar{P}_2^2) + 2g^{(2,2)} A^{(2,2)} \tau_2 \} / 15g, \quad (5.11)$$

$$B_2 = 8\omega_0 \bar{P}_2 \{ g^{(2,0)} A^{(2,0)} \tau_0(1-\bar{P}_2^2) - 2g^{(2,2)} A^{(2,2)} \tau_2 \} / 21g, \quad (5.12)$$

$$B_4 = 8\omega_0 \{ 3g^{(2,0)} A^{(2,0)} \tau_0 (\bar{P}_4 - \bar{P}_2^2) + g^{(2,2)} A^{(2,2)} \tau_2 \bar{P}_4 \} / 35g, \quad (5.13)$$

$$C_0 = \{ A^{(2,0)^2} \tau_0 (1 - \bar{P}_2^2) + 2A^{(2,2)^2} \tau_2 \} / 12, \quad (5.14)$$

$$C_2 = 13P_2 \{ A^{(2,0)^2} \tau_0 (1 - \bar{P}_2^2) - 2A^{(2,2)^2} \tau_2 \} / 84, \quad (5.15)$$

$$C_4 = \{ 3A^{(2,0)^2} \tau_0 (\bar{P}_4 - \bar{P}_2^2) + A^{(2,2)^2} \tau_2 \bar{P}_4 \} / 7. \quad (5.16)$$

In these equations ω_0 is the microwave frequency of the spectrometer, g is the g tensor, A is the hyperfine tensor and g is the partially averaged g factor (c.f. (4.51)). The correlation time τ_0 is associated with fluctuations in the orientation of the long axis of the spin probe and τ_2 with rotations about this axis. The expressions for the angular A coefficients differ slightly from those of Reference (52) which are in error.

McFarland and McConnell (137) were the first to attempt a calculation of the angular dependence of the linewidth resulting from rotational diffusion subject to an anisotropic ordering potential. However, it is difficult to compare their results with ours because they adopt a more general form for the correlation function. In fact they assume an exponential decay for $\phi_{q,p}(t)$ as in equation (5.7) but where the correlation time is taken to depend on q as well as on p . We shall not therefore attempt a comparison here.

Hemminga and Berendsen (140) have also implicitly employed the strong collision model in their calculation of the angular dependence of the linewidths for a spin probe. Their results are not directly comparable with equations (5.8) to (5.16) since they assume complete

ordering and neglect the pseudo-secular hyperfine terms in the dynamic spin hamiltonian. We can achieve some comparisons by setting both $\bar{P}_2$ and $\bar{P}_4$ equal to one in our equations. In this limit our results for the angular B coefficients are in complete accord with those obtained by Hemminga and Berendsen (140); there are however differences in the A and C coefficients. These result from their neglect of the pseudo-secular terms and so our results can be employed to gauge the magnitude of the errors resulting from this neglect. Thus their expressions for the angular A coefficients do not contain the contributions involving the hyperfine tensor and their C coefficients are, in our notation,

$$C_0 = 4A^{(2,2)^2}\tau_2/15, \quad (5.17)$$

$$C_2 = -8A^{(2,2)^2}\tau_2/21, \quad (5.18)$$

$$C_4 = 4A^{(2,2)^2}\tau_2/35. \quad (5.19)$$

We see then that ignoring the pseudo-secular terms creates considerable error in C_0 but is more successful for C_2 and C_4 .

We must now consider the analysis of the observed coefficients using the equations obtained from the strong collision model. Of the various parameters in equations (5.8) - (5.16) only three, τ_0, τ_2 and $\bar{P}_4$ are unknown. Thus the g and hyperfine tensors have been determined for (3-spiro- [2'-N-oxyl-3',3'-dimethyloxazolidine]) 5 α -androstan-17 β -ol, whose structure is virtually identical to that of the spin probe (136) and it is reasonable to employ these tensors. The components of the g tensor, in the coordinate system shown in figure 5.1, are

$$g_x = 2.0089,$$

$$g_y = 2.0058,$$

$$g_z = 2.0021,$$

and those for the nitrogen hyperfine tensor are

$$A_x = A_y = 101.78 \text{ Mrad.s}^{-1}$$

and $A_z = 540.35 \text{ Mrad.s}^{-1}.$

When calculating the irreducible components $F^{(2,p)}$ from these results it is important to realise that they are required in the coordinate system which contains the supposed molecular symmetry axis. Since the y axis makes an angle of about 20° with this symmetry axis the required components of the irreducible tensors are (120):

$$g^{(2,0)} = 0.0007, \quad A^{(2,0)} = -171.5 \text{ Mrad.s}^{-1},$$

$$g^{(2,2)} = -0.0032, \quad A^{(2,2)} = 216.1 \text{ Mrad.s}^{-1}.$$

The remaining parameter is the solute order $\bar{P}_2$ which is found to be 0.89 from the angular dependence of the hyperfine spacing. These parameters were then used to extract the two correlation times τ_0 and τ_2 as well as the solute order $\bar{P}_4$ from the three angular C coefficients with the results shown in Table 5.2. A second set of values was

determined from the B linewidth coefficients and these results are also included in Table 5.2.

TABLE 5.2 The strong collision parameters

Parameter	From B	From C
$\tau_0 / \text{s} \cdot \text{rad}^{-1}$	1.4×10^{-8}	3.9×10^{-8}
$\tau_2 / \text{s} \cdot \text{rad}^{-1}$	2.0×10^{-9}	2.4×10^{-9}
$\bar{P}_4$	0.63	0.73

There is reasonable agreement between these two sets although it is not possible, at this stage, to attribute the differences either to a failure of the strong collision model or to experimental error. The angular A linewidth coefficients have not been treated in this manner because they do contain a contribution resulting from unresolved proton hyperfine structure. We have however calculated the A coefficients using equations (5.8-10) and the two sets of parameters given in Table 5.2; these calculated coefficients are compared with the observed values in Table 5.3.

TABLE 5.3 The theoretical and experimental A coefficients ($\text{Mrad} \cdot \text{s}^{-1}$)

Coefficients	Experimental	From B	From C
A_0	52.7	32.8	54.0
A_2	-10.3	-14.0	-11.6
A_4	8.4	8.3	6.5

The calculated values of the A_2 and A_4 linewidth coefficients are in reasonable agreement with their experimental counterparts. In contrast there is a large discrepancy between the observed and mean predicted values of A_0 . However this difference, which is about 10 Mrad.s^{-1} , is comparable to the inhomogeneous line broadening caused by the unresolved proton hyperfine structure, and so does not indicate the presence of other relaxation processes.

One of the important consequences of such linewidth studies is the ability to determine the solute order $\bar{P}_4$ which is extremely difficult to determine in any other way. A knowledge of this additional parameter is important because it provides another test of the statistical theories of liquid crystal mixtures and, by implication of liquid crystals themselves. The cylindrical symmetry of both the spin probe and the smectic A phase dictate that the orientational energy of the probe is given by

$$U(\beta) = kT \sum_{\substack{L \\ \text{(even)}}} \lambda_L P_L(\cos\beta), \quad (5.20)$$

where β is the angle between the molecular symmetry axis and the director. According to theory (c.f. Section 4.4(b)) when the solute concentration is vanishingly small the expansion coefficients are

$$\lambda_L = u_L^{(12)} \bar{P}_L^{(1)} / kT, \quad (5.21)$$

where $\bar{P}_L^{(1)}$ is the solvent order and $u_L^{(12)}$ is a measure of the solute-

solvent interaction. The solute order $\bar{P}_L$ is obtained by taking the appropriate Boltzmann average:

$$\bar{P}_L = \frac{\int_0^\pi P_L(\cos\beta) \exp\{-U(\beta)/kT\} \sin\beta d\beta}{\int_0^\pi \exp\{-U(\beta)/kT\} \sin\beta d\beta} \quad (5.22)$$

Consequently if both $\bar{P}_2$ and $\bar{P}_4$ are known it should be possible to determine two of the expansion coefficients λ_L and so test the expected (118-120) convergence of equation (5.20). Unfortunately this determination is not possible when the solute order is high as we shall now discover.

If the orientational order is high, as it often is in a smectic phase, then the Boltzmann factor will be a rapidly decreasing function of β . Accordingly, in this high order limit, only small values of β make an important contribution to the integrand and we therefore obtain a simple expression for $\bar{P}_L$ by expanding the Legendre polynomials retaining terms up to β^2 . The potential energy becomes

$$\frac{U(\beta)}{kT} = \xi_0 + \xi\beta^2 \quad (5.23)$$

where

$$\xi = - \sum_L \sum_{r=0}^{L/2} (L/2 - r) \lambda_L a_{L,r} / kT, \quad (5.24)$$

(even)

and

$$a_{L,r} = \frac{(-1)^r (2L - 2r)!}{2^L r! (L-r)! (L-2r)!} \quad (5.25)$$

The ensemble averages $\bar{P}_L$ are independent of ξ_0 and so we shall not be concerned with its magnitude. Since the integrand is insensitive to high values of β the upper limit of the integrals may be extended to infinity and this then gives

$$\bar{P}_2 = 1 - 3/2\xi + O(\xi^{-2}), \quad (5.26)$$

and

$$\bar{P}_4 = 1 - 5/\xi + O(\xi^{-2}). \quad (5.27)$$

In this high order limit the magnitudes of both $\bar{P}_2$ and $\bar{P}_4$ are determined by the single parameter ξ and so there is apparently little to be gained from knowing $\bar{P}_4$ as well as $\bar{P}_2$. Notice as an example that equations (5.26), (5.27) are in complete accord with the asymptotic formulae (2.59) obtained for a simple Maier-Saupe potential such as

$$U(\beta) = \lambda_2 kT P_2(\cos\beta), \quad (5.28)$$

with $\lambda_2 = -2\xi/3$. In Table 2.1 we compared, not unfavourably, values of $\bar{P}_2$ and $\bar{P}_4$ obtained from the asymptotic formulae with values obtained from numerical integration. For example when ξ is 14 the approximate $\bar{P}_2$ is less than 1% too high while $\bar{P}_4$ is about 4% too small. The observed solute order of 0.89 corresponds to ξ equal to 13.0 and so the limiting relations for $\bar{P}_2$ and $\bar{P}_4$ should be relatively good. Indeed the value of $\bar{P}_4$ predicted by equation (5.27) is 0.62 which agrees well with the experimental values of 0.63 and 0.73. We may therefore conclude that $U(\beta)$ is indeed a rapidly decreasing function

of β as we might have anticipated.

The two correlation times, given in Table 5.2 show that the neglect of non-secular terms in deriving equations (5.8)-(5.16) is a valid approximation for this system for $\omega_0^2 \tau_0^2 > 1$ (52), although the extension to include these terms is quite straight forward (14). However it is difficult to comment further on these times since the strong collision model does not indicate how they should depend on the molecular structure or environment. In contrast the diffusion model does predict the dependence of the correlation functions on both the diffusion tensor and the orientational order and we shall now analyse our results in terms of these predictions.

5.5 The Diffusion Model

The solution of the rotational diffusion, in presence of an ordering potential, is usually expressed (96) in a basis of eigenfunctions of the diffusion operator for an isotropic potential. As mentioned in Section 4.4 (d), these eigenfunctions are just Wigner rotation matrices. This method of solution is clearly perfectly general but in practise the number of terms to be retained in the relevant series expansions (4.91), (4.93) increases as the system becomes more ordered and the potential more anisotropic. However in this case, Polnaszek et al. (98) have obtained a simple limiting solution. They start by a symmetrized version of the equation of motion (4.81) for the conditional probability, i.e.

$$-\frac{\partial}{\partial t} \hat{P}(\Omega_0 | \Omega t) = \hat{\Gamma} \hat{P}(\Omega_0 | \Omega t), \quad (5.29)$$

where $\hat{P}(\Omega_0|\Omega t) = P^{-\frac{1}{2}} P(\Omega_0|\Omega t)$, $\hat{\Gamma} = P^{-\frac{1}{2}} \Gamma P^{\frac{1}{2}}$ and $P \equiv P(\Omega)$ is the equilibrium angular distribution. The zeroth eigenfunction of $\hat{\Gamma} : G_0(\Omega)$ has a zero eigenvalue and is just

$$G_0(\Omega) = P^{\frac{1}{2}}. \quad (5.30)$$

A formal solution to equation (5.29) is

$$P(\Omega_0|\Omega t) = e^{-\hat{\Gamma}_0 \Omega t} P^{-\frac{1}{2}}(\Omega_0) \delta(\Omega - \Omega_0), \quad (5.31)$$

when the orientation at zero time is Ω_0 . Since the eigenfunctions of $\hat{\Gamma}$ form a complete set they may be used as a representation of the δ function and so

$$\hat{P}(\Omega_0|\Omega t) = P^{-\frac{1}{2}}(\Omega_0) \int_x e^{-E_x t} |X; \Omega\rangle \langle X; \Omega_0|, \quad (5.32)$$

where

$$G_x(\Omega) \equiv |X; \Omega\rangle. \quad (5.33)$$

The formalism used up to here can be applied to a quite general Markov process. As an example, it can include the strong collision model involving a single correlation time τ . In this case the eigenvalues of the stochastic operator are

$$E_x = (1 - \delta_{0x}) / \tau. \quad (5.34)$$

As another aside we can prove, before passing to describe the asymptotic solution, the simplification of the correlation function $\phi_{qpq'p'}$ in equation (5.3) to the ϕ_{qp} in equation (5.4). From the formal expression for the conditional probability we find

$$\phi_{qpq'p'}(t) = \sum_{x \neq 0} e^{-E_x t} \langle X; \Omega_0 | D_{q,p}^2(\Omega_0) | 0; \Omega_0 \rangle \langle 0; \Omega_0 | D_{q',p'}^{2*}(\Omega) | X; \Omega \rangle . \quad (5.35)$$

where the matrix notation, introduced by Polnaszek et al. (98) is defined by

$$\langle X; \Omega | f(\Omega) | X'; \Omega \rangle \equiv \int G_x^*(\Omega) f(\Omega) G_x(\Omega) d\Omega . \quad (5.36)$$

Since the rotation matrices form a complete set of functions which span the space of the Euler angles we can expand $|X; \Omega\rangle$ as

$$|X; \Omega\rangle = \sum_{L;m,n} a_{mn}^{XL} D_{m,n}^L(\Omega), \quad (5.37)$$

where

$$a_{mn}^{XL} = \langle D_{m,n}^L(\Omega) | X; \Omega \rangle . \quad (5.38)$$

Of course the eigenfunctions of $\hat{\Gamma}$ must transform according to an irreducible representation of the system which in this case is comprised of the liquid crystal and the spin probe. When both of these possess cylindrical symmetry the eigenfunctions are of the form

$$|X; \Omega\rangle = e^{im'\alpha} G_x(\beta) e^{in'\gamma}. \quad (5.39)$$

Consequently the expression for the eigenfunction in equation (5.37) reduces to

$$|X;\Omega\rangle = \sum_L a_{mn}^{XL} D_{m,n}^L(\Omega), \quad (5.40)$$

and the zeroth eigenfunction is simply

$$|0;\Omega\rangle = \sum_L a_{00}^{0L} D_{0,0}^L(\Omega). \quad (5.41)$$

The correlation function is then

$$\begin{aligned} \phi_{qpq'p'}(t) &= \sum_{x \neq 0} e^{-E_x t} \sum_{L, L', L'', L'''} a_{00}^{0L*} a_{mn}^{XL'} a_{mn}^{XL''*} a_{00}^{0L'''} \\ &\langle D_{0,0}^L(\Omega_0) | D_{q,p}^2(\Omega_0) | D_{m,n}^{L'}(\Omega_0) \rangle \langle D_{m,n}^{(L'')}(\Omega) | D_{q',p'}^{2*}(\Omega) | D_{0,0}^{L'''}(\Omega) \rangle. \end{aligned} \quad (5.42)$$

The matrix elements are just integrals of three rotation matrices and are given (34)

$$\langle D_{0,0}^L(\Omega_0) | D_{q,p}^2(\Omega_0) | D_{m,n}^{L'}(\Omega_0) \rangle = \frac{8\pi^2}{2L+1} \delta_{q+m,0} \delta_{p+n,0} C(L'2L;mq) C(L'2L;np) \quad (5.43)$$

and

$$\begin{aligned} \langle D_{m,n}^{L''}(\Omega) | D_{q',p'}^{2*}(\Omega) | D_{0,0}^{L'''}(\Omega) \rangle &= \\ \frac{8\pi^2(-1)^{q'-p'}}{2L''+1} \delta_{-q',m} \delta_{-p',n} C(L'''2L'';0-q') C(L'''2L'';0-p'). \end{aligned} \quad (5.44)$$

Combining the δ functions from these two matrix elements gives the desired result.

When the spin probe is not cylindrically symmetric the eigenfunctions of $\hat{\Gamma}$ take the form

$$|X; \Omega\rangle = e^{im'\alpha} G_x(\beta, \gamma). \quad (5.45)$$

Consequently the correlation function can only be reduced to

$$\phi_{qpq'p'}(t) = \phi_{qpq'p'}(t) \delta_{qq'} \quad (5.46)$$

for such a spin probe.

Let us return now to the asymptotic solution of equation (5.29). In view of equation (5.39) we may restrict our attention to the operator Γ_β

$$\begin{aligned} \Gamma_\beta = -D_1 \left\{ \frac{\partial^2}{\partial \beta^2} + \cot \beta \frac{\partial}{\partial \beta} - \frac{p^2 + q^2 - 2qp \cos \beta}{\sin^2 \beta} - \left(\frac{D_{11}}{D_1} - 1 \right) p^2 \right. \\ \left. + \frac{1}{kT} \sin \beta \frac{\partial}{\partial \beta} \left(\sin \beta \frac{dU(\beta)}{d\beta} \right) \right\}, \quad (5.47) \end{aligned}$$

which may be written as

$$\Gamma_\beta = -D_1 \left\{ \frac{\partial^2}{\partial \beta^2} + \frac{1}{\beta} \frac{\partial}{\partial \beta} - \frac{|p-q|^2}{\beta^2} - pq - \left(\frac{D_{11}}{D_1} - 1 \right) p^2 + 2\xi \left(2 + \beta \frac{\partial}{\partial \beta} \right) \right\} \quad (5.48)$$

in the limit of high order. This result is obtained using the complete expansion of the ordering potential; none the less it is identical in

form to the stochastic operator derived by Polnaszek et al. (98) who restricted the potential to just the first term. The eigenfunctions of this limiting form of Γ_β are found (98) to be

$$|M, p, q; \beta\rangle = \sqrt{(2\xi)^{-\nu}} N_M^\nu \exp(-\xi\beta^2) (\xi^{\frac{1}{2}}\beta)^{-\nu} L_M^\nu(\xi\beta^2), \quad (5.49)$$

where ν is $|p-q|$; the normalization factor is

$$N_M^\nu = \{2\xi^{-M} M! / (M + \nu)!\}^{\frac{1}{2}}, \quad (5.50)$$

and the function $L_M^\nu(\xi\beta^2)$ is a generalized Laguerre polynomial (80). The eigenvalues of the stochastic operator in the high-order limit are (98)

$$E_{M,\nu} = -\{2\xi^{-M} D_{-1} (2M+\nu) + pq D_{-1} + p^2 (D_{11} - D_{-1})\}. \quad (5.51)$$

The normalized distribution function obtained from equation (5.49) for the zeroth eigenfunction is

$$P_0(\beta) = 2\xi \exp(-\xi\beta^2), \quad (5.52)$$

which is, of course, identical to that resulting from the limiting form of the ordering potential given in equation (5.23). The matrix elements of the rotation matrices required to determine the correlation function $\phi_{q-p}(t)$ have been calculated by Polnaszek et al. (98); they find

$$\langle M, p, q; \Omega | D_{m', m}^{(L)} | M', p', q'; \Omega \rangle$$

$$\begin{aligned} &= \delta_{M, M'} \delta_{p, p'+m'} \delta_{q, q'+m} \delta_{v, v'} + \frac{1}{2\xi^{\frac{1}{2}}} \delta_{p, p'+m'} \delta_{q, q'+m} [\delta_{v, v'+1} (\delta_{M, M'}^{\sqrt{M+v}}) \\ &- \delta_{M, M'-1}^{\sqrt{M+1}}] + \delta_{v, v'-1} (\delta_{M, M'}^{\sqrt{M+v+1}} - \delta_{M, M'+1}^{\sqrt{M}}) [\delta_{m', m+1} f_+(M, m) \\ &- \delta_{m', m-1} f_-(M, m)], \end{aligned} \quad (5.53)$$

where

$$f_{\pm}(M, m) = \{ M(M+1) - m(m\pm 1) \}^{\frac{1}{2}}. \quad (5.54)$$

This expression for the matrix element differs from that in (5.23) where, presumably as the result of a printer's error, a factor $1/2\xi$ occurs instead of $1/2 \xi^{\frac{1}{2}}$.

We have evaluated the correlation functions $\phi_{q, -p}(t)$, required in the calculation of the angular linewidth coefficients, from equations (5.35), (5.49) and (5.51). The zero-frequency Fourier transforms $j_{q, -p}^{(0)}$ of these functions are given in Table 5.4; the terms with $p=\pm 1$ are not shown because the principal axes of the magnetic tensors are taken to be parallel to those of the diffusion tensor for this spin probe.

We can now calculate the angular linewidth coefficients in terms of the three non-zero spectral densities j_{10} , j_{12} and j_{22} ; the results are

$$\begin{aligned} A_0 &= 4\omega_0^2 \{ g^{(2,0)^2} j_{10} + g^{(2,2)^2} (j_{12} + j_{22}) \} / 15\bar{g}^2 \\ &+ I(I+1) \{ A^{(2,0)^2} j_{10} + A^{(2,2)^2} (j_{12} + j_{22}) \} / 10, \end{aligned} \quad (5.55)$$

$$\begin{aligned} A_2 &= 4\omega_0^2 \{ g^{(2,0)^2} j_{10} + g^{(2,2)^2} (j_{12} - 2j_{22}) \} / 21\bar{g}^2 \\ &+ I(I+1) \{ A^{(2,0)^2} j_{10} + A^{(2,2)^2} (j_{12} - 2j_{22}) \} / 28, \end{aligned} \quad (5.56)$$

TABLE 5.4 The spectral densities $j_{q,p}(0)$ for the diffusion model in the limit of high order.

q	p	$j_{q,p}(0)$
0	0	0
± 1	0	$3/4 \xi^2 D_1$
± 2	0	0
0	± 2	0
± 1	± 2	$1/2 \xi \{2D_{11} + (\xi - 1)D_1\}$
± 2	± 2	$1/4 D_{11}$

$$A_4 = -4\omega_o^2 \{4g^{(2,0)^2} j_{10} + g^{(2,2)^2} (4j_{12} - j_{22})\} / 35 \bar{g}^2 \\ + I(I+1) \{4A^{(2,0)^2} j_{10} + A^{(2,2)^2} (4j_{12} - j_{22})\} / 35, \quad (5.57)$$

$$B_0 = 8\omega_o \{g^{(2,0)} A^{(2,0)} j_{10} + g^{(2,2)} A^{(2,2)} (j_{12} + j_{22})\} / 15 \bar{g}, \quad (5.58)$$

$$B_2 = 8\omega_o \{g^{(2,0)} A^{(2,0)} j_{10} + g^{(2,2)} A^{(2,2)} (j_{12} - 2j_{22})\} / 21 \bar{g}, \quad (5.59)$$

$$B_4 = -8\omega_o \{4g^{(2,0)} A^{(2,0)} j_{10} + g^{(2,2)} A^{(2,2)} (4j_{12} - j_{22})\} / 35 \bar{g}, \quad (5.60)$$

$$C_0 = \{A^{(2,0)^2} j_{10} + A^{(2,2)^2} (j_{12} + j_{22})\} / 6, \quad (5.61)$$

$$C_2 = 13 \{A^{(2,0)^2} j_{10} + A^{(2,2)^2} (j_{12} - 2j_{22})\} / 84, \quad (5.62)$$

$$C_4 = - \{4A^{(2,0)^2} j_{10} + A^{(2,2)^2} (4j_{12} - j_{22})\} / 7. \quad (5.63)$$

Although the angular linewidth coefficients are a function of three spectral densities there are only two unknowns namely the principal

components of the diffusion tensor. Consequently the problem is over determined when all three components of an angular linewidth coefficient are known. We have therefore sought to obtain the best values for D_{11} and D_{11} in the following way. The three spectral densities cannot be evaluated from either the B or the C coefficients because the determinant of the appropriate coefficients vanishes. We therefore define new variables which for the C linewidth coefficients are

$$a = A^{(2,2)^2} j_{22} \quad , \quad (5.64)$$

$$\text{and } b = A^{(2,0)^2} j_{10} + A^{(2,2)^2} j_{12} \quad ; \quad (5.65)$$

similar variables are employed in the analysis of the B coefficients. The best values for a and b are now obtained from the linewidth coefficients using a linear least squares fit. As a check we use these least-squares fitted parameters to recalculate the coefficients; the results of such calculations are given in Table 5.5. The agreement between theory and

TABLE 5.5 The observed and calculated values for the angular B and C linewidth coefficients

Component L				
	Observed	Calculated	Observed	Calculated
0	-24.2	-24.1	40.1	25.3
2	24.6	24.6	-11.2	-21.0
4	-0.6	-0.6	-12.8	-18.2

experiment is extremely good for the B coefficients but clearly less impressive for the C linewidth coefficients; we shall return to this discrepancy shortly. Given the value for the variable a the spectral

density j_{22} can be calculated and from this we can evaluate the parallel component of the diffusion tensor. Armed with this component it is possible to extract the other component $D_{\perp}$ from a knowledge of b . The values obtained for $D_{\parallel}$ and $D_{\perp}$ from both the B and C linewidth coefficients are given in Table 5.6. The agreement between the values extracted from the two sets of linewidth coefficients is encouraging; we shall return to the large anisotropy in the diffusion tensor shortly.

TABLE 5.6 The diffusion tensor

Diffusion tensor	From B	From C
$D_{\parallel}$ (Mrad s ⁻¹)	137	122
$D_{\perp}$ (Mrad s ⁻¹)	2.6	2.6
$D_{\parallel} / D_{\perp}$	53	46

As a check on the validity of the diffusion model, in the limit of high order, the components of the diffusion tensor, given in Table 5.6, have been used to calculate two sets of the angular A linewidth coefficients. The results of these calculations are listed in Table 5.7 together with the experimental values of A_L . The agreement with experiment is seen to

TABLE 5.7 The experimental and theoretical A linewidth coefficients (Mrad s⁻¹)

Coefficient	Experimental	From B	From C
A_0	52.7	33.0	35.6
A_2	-10.3	-13.8	-16.0
A_4	8.4	8.8	8.2

be good especially as the inhomogeneous broadening caused by unresolved proton hyperfine structure might be expected to make a contribution of about 15 Mrad.s^{-1} to A_0 . On balance this limiting form of the diffusion model appears to provide the most satisfactory quantitative interpretation of all three experimental linewidth coefficients. However, it may be significant that the asymptotic spectral densities calculated with this Polnaszek et al (98) method appear not to satisfy all the symmetry requirements (96,129). This important problem is now under investigation. It would be unwise to attempt to differentiate between the two models on the basis of our experimental results. However one clear advantage of the diffusion model is that the dynamic parameters occurring in the theory may then be the subject of further rationalisation. We shall now attempt such an analysis.

A combination of experimental (145) and theoretical (143) investigations has shown that the principal components of the diffusion tensor are often given by (147):

$$D_i = kT/8\pi\eta\sigma_i\kappa_{ii} \quad . \quad (5.66)$$

In this expression σ_i is a geometric factor which takes the values (124)

$$\sigma = 4r_x^2 (r_z^2 - r_x^2)/3(2r_z - r_x^2S) \quad , \quad (5.67)$$

$$\text{and } \sigma = 4(r_z^4 - r_x^4)/3\{(2r_z^2 - r_x^2)S - 2r_z\} \quad , \quad (5.68)$$

for a symmetric top molecule with semi-axes $r_z > r_x = r_y$ and where

$$S = 2(r_z^2 - r_x^2)^{-\frac{1}{2}} \log_e \{ [r_z + (r_z^2 - r_x^2)^{\frac{1}{2}}] / r_x \} \quad . \quad (5.69)$$

The parameter η has the dimensions of viscosity and is frequently identified with the coefficient of shear viscosity. When κ is the unit tensor then equation (5.66) is the expression obtained by Perrin (124) for

the diffusion tensor of a symmetric top in the hydrodynamic limit.

Experimentally κ is observed to deviate from unity; it is however found to be independent of both temperature and pressure although markedly solvent dependent (147). These results have been rationalised by a theory (146) which relates κ to the intermolecular torque T and the intermolecular force F , in fact according to this theory

$$\kappa_{ii} = (3/4r_o^2) (\overline{T_i^2}/\overline{F^2}) \quad , \quad (5.70)$$

where r_o is the effective hydrodynamic radius of the spin probe. The tensor κ may be referred to as the anisotropic interaction tensor since its magnitude is determined by the anisotropy in the intermolecular potential which governs the torques whereas the force depends on the total intermolecular potential. The ratio of the components of the diffusion tensor is therefore

$$D_{||}/D_{\perp} = \sigma_{\perp} \kappa_{\perp} / \sigma_{||} \kappa_{||} \quad , \quad (5.71)$$

which should be independent of temperature and pressure but not solvent.

The application of this result to liquid crystals implies that the viscosity η occurring in equation (5.66) for the diffusion tensor is a scalar. At first sight such an approximation might be thought to be rather poor for the coefficient of shear viscosity for a nematic mesophase is found to be highly anisotropic (6). However this need should not be so for it should be recalled that the shear viscosity is a translational property whereas the diffusion tensor relates to the rotational motion. In addition any attempt to allow for an anisotropy in η would introduce a largely arbitrary parameter into the problem. The ratio $\sigma_{\perp} / \sigma_{||}$ can be calculated provided the molecular dimensions are known and we have estimated them with the aid of molecular models; r_z is about 11.5 Å and

r_x is approximately $3.5 \text{ \AA}$. These dimensions yield a value for $\sigma_{\perp} / \sigma_{\parallel}$ of about 3 and so the ratio $\kappa_{\perp} / \kappa_{\parallel}$ of the components of the anisotropic interaction tensor is approximately 17. This value is large and will naturally depend on the choice of the molecular dimensions, however these and hence the ratio $\kappa_{\perp} / \kappa_{\parallel}$ are unlikely to be in serious error. Theoretically the maximum value of κ is unity and this occurs when the intermolecular potential is dominated by the anisotropic component (146). At the other extreme κ is zero which corresponds to a purely isotropic intermolecular potential. Accordingly the value of 17 implies that κ is no larger than 0.06; in other words rotation about the long molecular axis is essentially unhindered. This result is in accord with the cylindrical symmetry of the ordering matrix observed for this spin probe dissolved in several nematic mesophases (120).

Also, a recent independent work by Hemminga (128) on the same spin probe in a highly ordered ($\bar{P}_2 \approx 0.85$) lyotropic system seems to confirm that $D_{\parallel} / D_{\perp}$ is between 40 and 50, and then that κ is very small.

It is possible to check the ratio $D_{\parallel} / D_{\perp}$ by measuring the relative linewidth coefficients when the spin probe is dissolved in the isotropic melt of the mesogen. We have made these measurements and find that C/B is approximately -2.1 and independent of temperature. This ratio is related to $D_{\parallel} / D_{\perp}$ by

$$\frac{C}{B} = \frac{15g\{A^{(2,0)^2}(2D_{\parallel}/D_{\perp} + 1)/3 + 2A^{(2,2)^2}\}}{48\omega_o\{g^{(2,0)}A^{(2,0)}(2D_{\parallel}/D_{\perp} + 1)/3 + 2g^{(2,2)}A^{(2,2)}\}}, \quad (5.72)$$

provided the molecular motion is sufficiently slow to make the non-secular contributions to the linewidth negligible (126). By using the same components of the anisotropic g and nitrogen hyperfine tensor as those encountered previously the ratio $D_{\parallel} / D_{\perp}$ is calculated to be 44. This

result, is in excellent agreement with the value determined for the spin probe dissolved in the smectic phase especially as $D_{||}/D_{\perp}$ is rather sensitive to the magnitude of C/B. The close similarity in the ratios for the two phases is unexpected in view of the absence of any long range orientational order in the isotropic phase which might be expected to reduce κ in this phase. Our results for $D_{||}/D_{\perp}$ presumably imply that κ is determined by the local molecular environment which is essentially unchanged on passing from the smectic to the isotropic phase. Accordingly if this interpretation is correct then $D_{||}/D_{\perp}$ should be reduced when the solvent is composed of molecules more symmetric than those of the mesogen. We have therefore measured the ratio of C/B for the spin probe dissolved in o-terphenyl and find it to be -1.7. This corresponds to the smaller value for $D_{||}/D_{\perp}$ of 19 and such a reduction is in accord with our expectations.

It is appropriate, in concluding, to comment on those areas in which the theory has been less successful. For example the predicted angular dependence of the B linewidth coefficient is in complete accord with experiment whereas the agreement for the C coefficient was not so impressive. Similarly the diffusion model was able to provide an almost quantitative account of the angular B coefficients but only a qualitative description of the C linewidth coefficients. These discrepancies can be ascribed to two assumptions in the analysis; the first is implicit and the second explicit. We have assumed implicitly that the director is uniformly aligned throughout the sample of the smectic mesophase. However minor deviations from complete alignment could result when the smectic phase is formed from the aligned nematic mesophase. Indeed the slight asymmetry in the spectral line shape hints at such deviations in uniformity (52,148). To first order the imperfect alignment produces inhomogeneous broadening

of the spectral lines. For a nitroxide spin probe the contribution of such broadening to the B coefficient depends on the anisotropy in the partially averaged g tensor $\tilde{g}$ whereas the contribution to C is determined by the anisotropy in the partially averaged hyperfine tensor $\tilde{A}$ (52). Experimentally $\tilde{g}$ is found to be virtually isotropic for this system whereas $\tilde{A}$ is highly anisotropic. Consequently the inhomogeneous line broadening will alter the angular C linewidth coefficients but not the B coefficients. In addition the angular dependence of C resulting from inhomogeneous line broadening is predicted to be different from that caused by spin relaxation (52). The behaviour of the B linewidth coefficient is therefore expected to be in better accord with theory than that of the C coefficient.

The explicit assumption concerns the quantization of the nuclear spin in the direction of the magnetic field. This approximation is exact when the magnetic field is either parallel or perpendicular to the director but is least reliable when the field is midway between these two extremes as we shall discuss in the next Chapter. In addition the assumption is less accurate when there is a large anisotropy in the partially averaged hyperfine tensor. Again the consequences produced by the inaccuracy of the assumption will affect the C rather than the B coefficients and will have a different angular dependence to that given e.g. in equation (5.6).

CHAPTER SIX

A MORE COMPLETE THEORY OF ANGULAR DEPENDENT LINEWIDTHS

6.1 Introduction

The theory of angular dependent linewidths employed in the last Chapter was based on an explicit assumption, namely that when the angle between director and magnetic field is varied, the nuclear spin is still quantized along the direction of the magnetic field. This is equivalent to neglecting the effect on the linewidths of the pseudosecular hyperfine terms in the static hamiltonian. The existence of the problem has been pointed out in the literature (137) but the effect has simply been disregarded as we did in the previous Chapter. Part of the reason for doing so is probably the absence of a simple theory for the effect. In this Chapter we shall develop such a theory, showing that the linewidths can still be expressed as

$$T_2^{-1}(m) = A + Bm + Cm^2. \quad (6.1)$$

However, the angular dependent coefficients A,B,C can no longer be written in the simple form

$$X(\gamma) = X_0 + X_2 P_2(\cos\gamma) + X_4 P_4(\cos\gamma) \quad (6.2)$$

where $X = A, B, C$.

6.2 Theory

We shall start by reconsidering briefly the static hamiltonian for a spin probe reorienting rapidly in a liquid crystal. Fast reorientation is intended here in the sense that Redfield (100) type theories (c.f. Chapter 4) are applicable. In a molecule fixed coordinate system the spin hamiltonian is, in irreducible tensor notation,

$$H = \sum_{\mu; L, p} (-)^p F_{\mu}^{(L, p)} T_{\mu}^{(L-p)}, \quad (6.3)$$

where, as in the previous Chapters, the F_{μ} and T_{μ} are the relevant magnetic and spin tensors. A transformation of T_{μ} to the director frame confines the time dependence to a Wigner rotation matrix. A further transformation to a coordinate system with the z axis parallel to the static magnetic field gives the spin hamiltonian at time t as:

$$H(t) = \sum (-)^p F_{\mu}^{(L, p)} D_{q, -p}^L(t) D_{r, q}^L(\Omega) T_{\mu}^{(L, r)}. \quad (6.4)$$

An ensemble average gives, for a uniaxial mesophase, the static hamiltonian as

$$\bar{H} = \sum (-)^p F_{\mu}^{(L, p)} \overline{D_{q, -p}^L} \delta_{q0} D_{r, q}^L(\Omega) T_{\mu}^{(L, r)} \quad (6.5)$$

$$= \sum \tilde{F}_{\mu}^{(L, 0)} D_{r, 0}^L T_{\mu}^{(L, r)}, \quad (6.6)$$

where the partially averaged tensors $\tilde{F}_{\mu}^{(L, 0)}$ are, as usual,

$$\tilde{F}_{\mu}^{(L,0)} \equiv \sum (-)^p F_{\mu}^{(L,p)} \overline{D_{0,-p}^L} \quad (6.7)$$

The eigenvalues of the spin hamiltonian (6.6) determine the line positions and its eigenfunctions constitute the basis to be used in the calculation of the Redfield matrix elements. For a nitroxide spin probe the so called high-field approximation, which amounts to neglecting that part of the static spin hamiltonian which does not commute with S_z , can usually be invoked (109, 116). We shall then neglect terms such as $S_{\pm}I_{\pm}$, $S_{\pm}I_z$, $BS_{\pm}$, i.e. the non-secular terms, when considering the irreducible spin operators. In Table 6.1 we give the explicit expressions for these spin operators and their corresponding spatial tensors. An inspection of the spin hamiltonian matrix in the product basis $|S m_S\rangle |I m_I\rangle$ shows that it is justified to neglect the non-secular terms as long as the partially averaged hyperfine terms are much smaller than the transition frequency. We shall call the static hamiltonian, after the elimination of the non-secular terms, the truncated hamiltonian. The time-independent transformation $D_{r,0}^L(\Omega)$ connecting director and field involves in principle two Euler angles. However, in view of the cylindrical symmetry about the director and field, it is sufficient to consider only angle between the z axis of the two frames, i.e. $D_{r,0}^L(0\gamma 0)$ where γ is the angle between the director and the static magnetic field. From equation (6.5) it is easy to see that if $\gamma=0$ or $\gamma=\pi/2$ the truncated hamiltonian is already diagonal, since

$$\begin{aligned} D_{r,0}^2(000) &= \delta_{r0} \\ D_{r,0}^2(0 \frac{\pi}{2} 0) &= -\frac{1}{2} \delta_{r0} + \sqrt{\frac{3}{8}} \delta_{r2} \end{aligned} \quad (6.8)$$

TABLE 6.1 The irreducible components of the Zeeman and hyperfine tensors g and A together with that of their corresponding spin operators. It has been assumed that the magnetic field $B = B(001)$.

$$g^{(0,0)} = \sqrt{3} g$$

$$T_g^{(0,0)} = -B S_z / \sqrt{3}$$

$$g^{(2,0)} = \sqrt{3}/2 g'_{zz}$$

$$T_g^{(2,0)} = \sqrt{2}/3 B S_z$$

$$g^{(2,\pm 1)} = \mp (g'_{xz} \pm i g'_{yz})$$

$$T_g^{(2,\pm 1)} = \mp (B S_{\pm})/2$$

$$g^{(2,\pm 2)} = (g'_{xx} - g'_{yy} \pm 2i g'_{xy})/2$$

$$T_g^{(2,\pm 2)} = 0$$

$$A^{(0,0)} = \sqrt{3} a$$

$$T_A^{(0,0)} = S \cdot I / \sqrt{3}$$

$$A^{(2,0)} = \sqrt{3}/2 A'_{zz}$$

$$T_A^{(2,0)} = \sqrt{2}/3 [S_z I_z - (S_+ I_- + S_- I_+)/4]$$

$$A^{(2,\pm 1)} = \mp (A'_{xz} \pm i A'_{yz})$$

$$T_A^{(2,\pm 1)} = \mp (I_{\pm} S_z + I_z S_{\pm})/2$$

$$A^{(2,\pm 2)} = (A'_{xx} - A'_{yy} \pm 2i A'_{xy})/2$$

$$T_A^{(2,\pm 2)} = I_{\pm} S_{\pm} / 2$$

(a) The prime indicates the traceless tensor components.

Therefore, when the director is either parallel or perpendicular to the magnetic field B , the set $|S=1/2, m_S\rangle |I=1, m_I\rangle$ is a good basis set and can be employed for the calculation of the Redfield matrix. However, when $0 < \gamma < \pi/2$, the situation is far more complicated. In fact an inspection of the truncated hamiltonian shows that it is not diagonal i.e. it does not commute with $S_z I_z$ any more. Its matrix consists of two 3×3 blocks corresponding to $m_S = \pm 1/2$. The off-diagonal elements in the two blocks are the pseudosecular hyperfine terms. As far as the static hamiltonian is concerned the problem is formally identical to that occurring in single crystal studies of the hyperfine structure of a radical spectrum (114, 150). There one has essentially two possibilities. One is to express the eigenfunctions of the truncated $\bar{H}(\gamma)$ in terms of the eigenfunctions of $\bar{H}(0)$ as

$$|I_n\rangle' = \sum_m |I_m\rangle D_{m,n}^I$$

using the fact that the eigenfunctions of an angular momentum (spin) I transform according to the irreducible representation $D^{(I)}$ (151). The other, equivalent, possibility is to notice that terms such as $S_z I_{\pm}$ can be eliminated by changing to a new set of axes for the nuclear spin I (114). Since the partially averaged hyperfine tensor has cylindrical symmetry, Q , the direction of quantization of I lies in the plane defined by the director d and the field B (114). In figure 6.1 the various relevant directions are shown. The angle χ between Q and B is so defined that the coefficients in front of terms like $S_z I_{\pm}$ in the static hamiltonian vanish after the transformation. The explicit

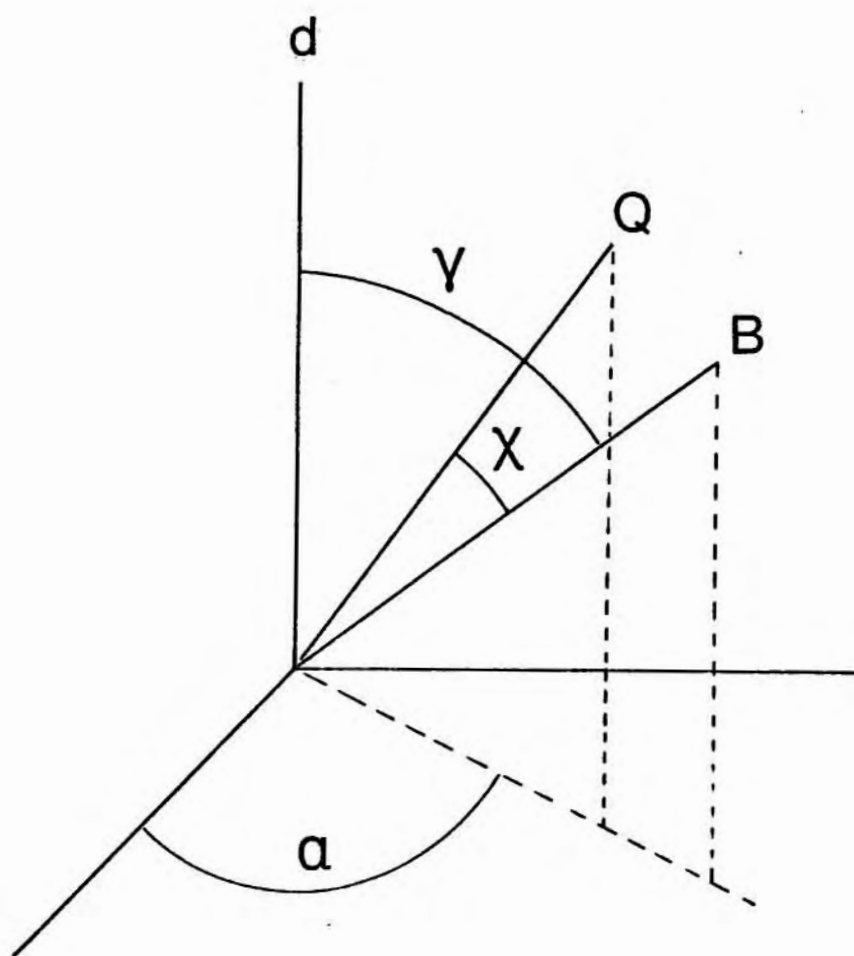


Figure 6.1 The axes systems involved in the treatment of the nuclear spin quantization effect. In the figure, d represents the director, Q the axis of quantization of the nuclear spin, B the direction of the static magnetic field.

expression for χ is given by (114,137)

$$\begin{aligned}\cos\chi &= \{\tilde{g}_\perp \tilde{A}_\perp \sin^2\gamma + \tilde{g}_\parallel \tilde{A}_\parallel \cos^2\gamma\} / \tilde{g} \tilde{a} , \\ \sin\chi &= \{\tilde{g}_\perp \tilde{A}_\perp - \tilde{g}_\parallel \tilde{A}_\parallel\} \sin\gamma \cos\gamma / \tilde{g} \tilde{a} ,\end{aligned}\tag{6.9}$$

where

$$\tilde{g}^2 \tilde{a}^2 = (\tilde{g}_\parallel^2 \tilde{A}_\parallel^2 - \tilde{g}_\perp^2 \tilde{A}_\perp^2) \cos^2\gamma + \tilde{g}_\perp^2 \tilde{A}_\perp^2 .\tag{6.10}$$

This results can be further simplified by assuming that the partially averaged g tensor is essentially isotropic, an approximation expected to be very good for all the practical cases we have to deal with (52). This assumption has also the important consequence that as we change the angle γ the electron spin is constantly quantized along the field. The nuclear spin quantization axis, instead, changes as the angle γ changes and it deviates most from the field direction when

$$\cos^2\gamma = (\tilde{A}_\parallel \tilde{A}_\perp - \tilde{A}_\perp^2) / (\tilde{A}_\parallel^2 - \tilde{A}_\perp^2) .\tag{6.11}$$

At this point

$$\cos\chi = \cos\chi_{\max} = 2\tilde{A}_\perp^2 / \{(\tilde{A}_\parallel + \tilde{A}_\perp)(\tilde{A}_\parallel \tilde{A}_\perp)^{\frac{1}{2}}\} .\tag{6.12}$$

The magnitude of the effect clearly depends on the anisotropy in the partially averaged hyperfine tensor and is therefore related to the order parameter. For example, for a spin probe like the one used in the previous Chapter (see figure 5.1), with the symmetry

axis of A perpendicular to the long axis of the molecule, we have

$$\tilde{A} = a - \frac{1}{2} A'_{\parallel} \bar{P}_2 \quad (6.13)$$

$$\tilde{A} = a + \frac{1}{4} A'_{\parallel} \bar{P}_2$$

and therefore $(\tilde{A}_{\parallel} - \tilde{A}_{\perp}) = -3A'_{\parallel} \bar{P}_2/4$, where $\bar{P}_2$ gives the orientational order of the long molecular axis and $A'_{\parallel}$ is the component of the traceless hyperfine tensor parallel to its symmetry axis. The problem so far has been mainly an adaptation of known results, but of course in liquid crystals as compared to single crystals the interesting thing is that we have also anisotropic dynamic effects. To investigate the effect that the proper quantization of the nuclear spin has on the electron resonance spectrum we return to the time dependent spin hamiltonian in equation (6.4) and rewrite it more explicitly as

$$\begin{aligned} H(t) = H^{(0)} + \sum (-)^p g^{(2,p)} D_{q,-p}^2(t) D_{r,q}^2(\gamma) T_g^{(2,r)} \\ + \sum (-)^p A^{(2,p)} D_{q,-p}^2(t) D_{r,q}^2(\gamma) T_A^{(2,r)}, \end{aligned} \quad (6.14)$$

where $H^{(0)}$ is the scalar part of the hamiltonian. Now we decouple T_A in its spin operator components (34)

$$T_A^{(2,r)} = \sum_n C(112;n,r-n) S^{(1,n)} I^{(1,r-n)}, \quad (6.15)$$

and reject the non-secular terms. Then

$$T_A^{(2,r)} = C(112;0r) S^{(1,0)} I^{(1,r)}. \quad (6.16)$$

We then transform I to its quantization frame which we indicate with an upper cap,

$$T_A^{(2,r)} = C(112, 0r) S^{(1,0)} \sum_m D_{m,r}^1(\chi) \hat{I}^{(1,m)}. \quad (6.17)$$

Substitution in equation (6.14) gives the truncated spin hamiltonian as

$$\begin{aligned} H(t) = H^{(0)} + \sum (-)^p g^{(2,p)} D_{q,-p}^2(t) D_{r,q}^2(\gamma) T_g^{(2,r)} \delta_{r0} \quad (6.18) \\ + \sum (-)^p A^{(2,p)} D_{q,-p}^2(t) D_{r,q}^2(\gamma) D_{m,r}^1(\chi) C(112; 0r) S^{(1,0)} \hat{I}^{(1,m)}. \end{aligned}$$

When we take an ensemble average the rotation of χ causes only the $m=0$ term to survive in the 2nd line of equation (6.18)

$$\begin{aligned} \bar{H} = H^{(0)} + \sum (-)^p g^{(2,p)} \overline{D_{0,-p}^2} D_{0,0}^2(\gamma) T_g^{(2,0)} \quad (6.19) \\ + \sum (-)^p A^{(2,p)} \overline{D_{0,-p}^2} D_{r,0}^2(\gamma) D_{0,r}^1(\chi) C(112; 0r) S^{(1,0)} I^{(1,0)}. \end{aligned}$$

The dynamic spin hamiltonian is

$$\begin{aligned} H_1(t) = H(t) - \bar{H} \\ = \sum_m \left[\sum_{p,q,r} (-)^p g^{(2,p)} \{ D_{q,-p}^2(t) - \overline{D_{0,-p}^2} \delta_{0q} \} D_{r,q}^2(\gamma) \delta_{r0} \delta_{mr} \right] T_g^{(2,m)} \\ + \sum_m \left[\sum_{p,q,r} (-)^p A^{(2,p)} \times \{ D_{q,-p}^2(t) - \overline{D_{0,-p}^2} \delta_{0q} \} D_{r,q}^2(\gamma) \right. \\ \left. \times \frac{C(112; 0r)}{C(112; 0m)} D_{m,r}^1(\chi) \right] T_A^{(2,m)} \quad (6.20) \end{aligned}$$

where we have written

$$\hat{T}_A^{(2,m)} \equiv C(112,0m) S^{(1,0)} \hat{I}^{(1,m)},$$

as a tensor formally analogous to the truncated hyperfine tensor (6.16).

With this definition we may now write the dynamic hamiltonian as

$$H_1(t) = \sum_m (-)^m F_\mu^{(2,-m)} \hat{T}_\mu^{(2,m)}. \quad (6.21)$$

Since the $|S m_S\rangle |\hat{I} m_I\rangle$ basis is a good basis and since the hamiltonian (6.21) is formally identical to that of the ordinary nitroxide problem (52) it follows that the linewidths are still given by the usual expression (6.1), with the coefficients A,B,C given by equations (4.62)-(4.64) in terms of the spectral densities $J_r^{\mu\mu'}$. The tensors $F_\mu^{(2,-m)}$ in equation (6.21) are given by

$$F_g^{(2,-m)} = \sum_{p,q} (-)^p g^{(2,p)} \{ D_{q,-p}^2(t) - \overline{D_{0,-p}^2} \delta_{0q} \} D_{0,q}^2(\gamma) \delta_{m0}, \quad (6.22)$$

$$F_A^{(2,-m)} = \frac{(-)^m}{C(112,0m)} \sum_{p,q,r} (-)^p A^{(2,p)} \{ D_{q,-p}^2(t) - \overline{D_{0,-p}^2} \delta_{0q} \} \quad (6.23)$$

$$D_{r,q}^2(\gamma) C(112,0r) D_{m,r}^1(\chi).$$

This leads to the following spectral densities

$$J_O^{gg} = \sum g^{(2,p)} g^{(2,p)*} \{ d_{0,q}^2(\gamma) \}^2 j_{q-p}, \quad (6.24)$$

$$J_0^{gA} = \sqrt{\frac{3}{2}} \sum g^{(2,p)} A^{(2,p)*} d_{0,q}^2(\gamma) d_{r,q}^2(\gamma) C(112,0r) d_{0,r}^1(\chi) j_{q-p} \quad (6.25)$$

$$J_m^{AA} = \frac{1}{C(112,m0)^2} \sum A^{(2,p)} A^{(2,p)*} d_{r,q}^2(\gamma) d_{r',q}^2(\gamma) C(112,0r) C(112,0r') d_{m,r}^1(\chi) d_{m,r'}^1(\chi) j_{q-p} \quad (6.26)$$

or

$$J_m^{AA} = \frac{1}{C(112,m0)^2} \sum_p A^{(2,p)} A^{(2,p)*} \sum_q j_{q-p} \left\{ \sum_{r=-1} d_{r,q}^2(\chi) d_{m,r}^1(\chi) C(112,0r) \right\}^2 \quad (6.27)$$

It is easy to check that when there is no nuclear spin quantization effect, i.e. $\chi=0$ these spectral densities reduce to the ordinary ones (c.f. Chapter 4). In particular when the director is parallel or perpendicular to the field the spectrum is unchanged. The spectral densities (6.24-6.27) show also that another important feature of the angular dependent linewidth coefficients is unchanged i.e. they still possess the symmetry

$$X(\gamma) = X(\pi-\gamma), \quad (6.28)$$

where $X=A,B,C$. This can be easily verified from the fact that $\chi(\gamma)=-\chi(\pi-\gamma)$ and from the symmetry properties of the Wigner rotation matrices and the Clebsch-Gordan coefficients (34). In general it is no longer possible to write the linewidth coefficients in the form (6.2) as we did in the previous Chapter but, in view of the symmetry in equation (6.28), it is possible to expand the coefficients $X(\gamma)$

in a series of even Legendre polynomials as

$$X(\gamma) = \sum_L X_L P_L(\cos\gamma) \quad , \quad L \text{ even} \quad (6.29)$$

Therefore the angular dependence in equation (6.2) can be regarded as a special case of equation (6.29) where the series terminates on the $L = 4$ term.

6.3 Results

To investigate the effect that the non-quantization of the nuclear spin along the magnetic field has on the linewidths we have performed a set of model calculations for a nitroxide spin probe with various order parameters. We have employed the same magnetic parameters as those used before (cf. page 118) for the cholestane spin probe whose structure is shown in figure 5.1. As far as the dynamic part of the problem is concerned, we have used the strong collision spectral densities given in Table 4.1, with the following correlation times:

$$\begin{aligned} \tau_0 &= 5. \times 10^{-9} \text{ s/rad} \\ \tau_2 &= 1. \times 10^{-9} \text{ s/rad} \end{aligned}$$

In figures (6.2) - (6.4) we compare the angular coefficients $A(\gamma)$, $B(\gamma)$, $C(\gamma)$ obtained by allowing for the non-quantization effect with those obtained by neglecting this effect ($\chi = 0$). The order parameters employed were $\bar{P}_2 = 0.9, 0.8, 0.6$, respectively, while the parameter $\bar{P}_4$ was obtained assuming a Maier-Saupe pseudopotential (cf. Table 2.1).

It is apparent that the effect is most important for the A and C coefficients as we had anticipated in Chapter 5. Therefore, in general, the order parameter $\bar{P}_4$ extracted from the B coefficients is likely to be more accurate than that obtained from the C, if the non-quantization effect

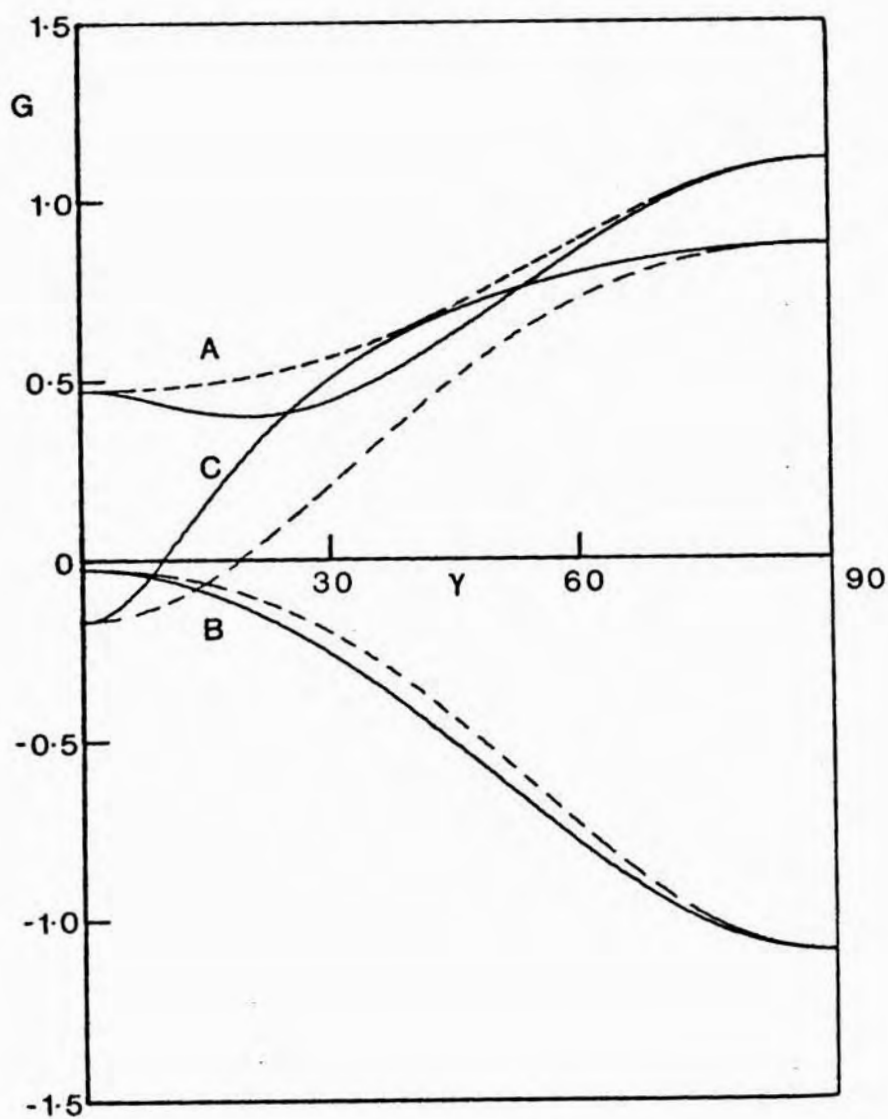


Figure 6.2 The angular dependent linewidth coefficients $A(\gamma)$, $B(\gamma)$, $C(\gamma)$ calculated considering the non-quantization effect (continuous line) and neglecting it (dashed line). $\bar{P}_2 = 0.90$, $\bar{P}_4 = 0.71$, $\tau_0 = 5. \times 10^{-9}$ s/rad, $\tau_2 = 1. \times 10^{-9}$ s/rad.

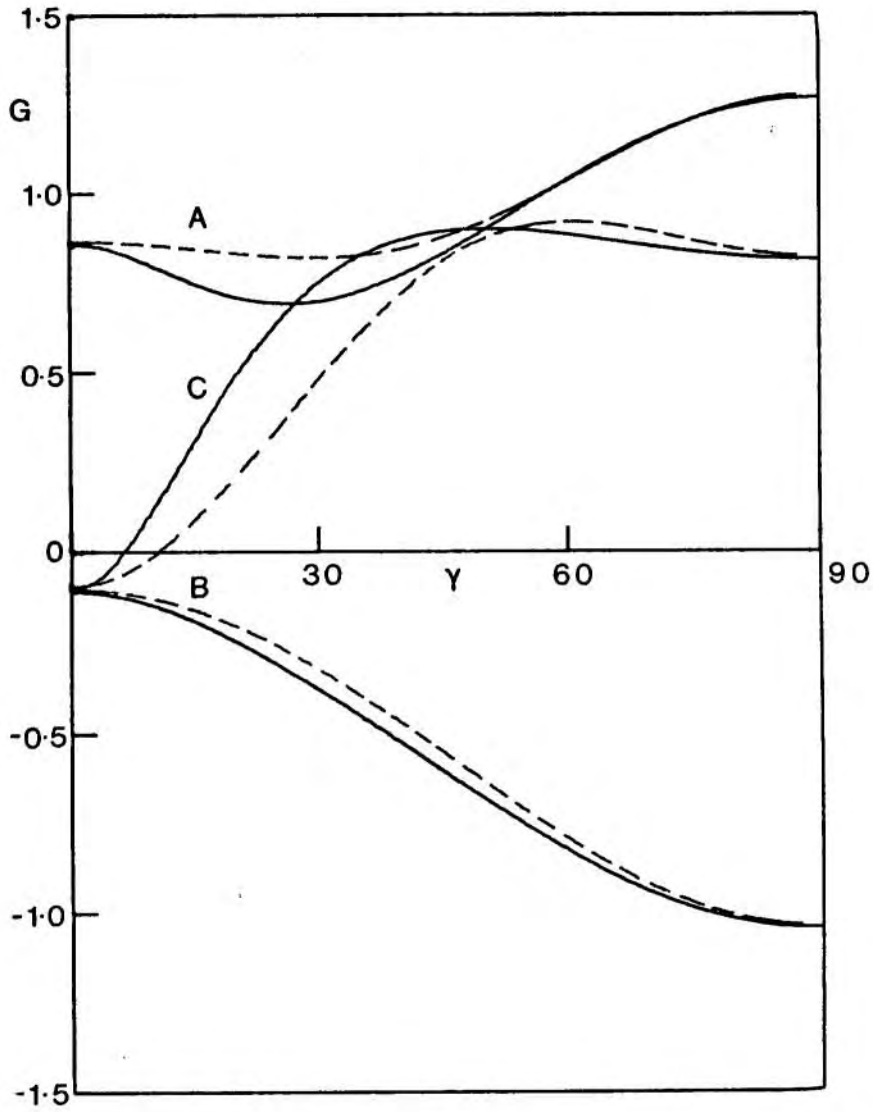


Figure 6.3 The angular dependent linewidth coefficients $A(\gamma)$, $B(\gamma)$, $C(\gamma)$ calculated considering the non-quantization effect (continuous line) and neglecting it (dashed line). $\bar{P}_2 = 0.79$, $\bar{P}_4 = 0.48$, $\tau_0 = 5. \times 10^{-9}$ s/rad, $\tau_2 = 1. \times 10^{-9}$ s/rad.

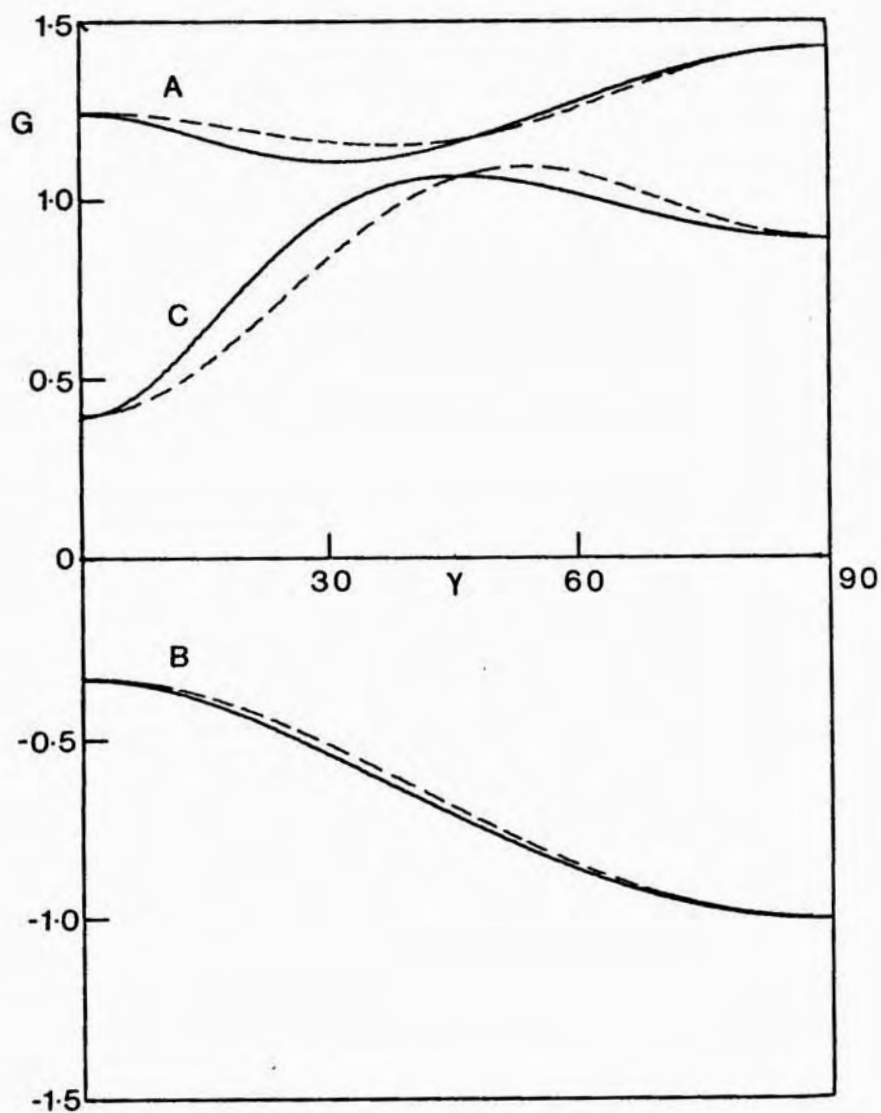


Figure 6.4 The angular dependent linewidth coefficients $A(\gamma)$, $B(\gamma)$, $C(\gamma)$ calculated considering the non-quantization effect (continuous line) and neglecting it (dashed line). $\bar{P}_2 = 0.60$, $\bar{P}_4 = 0.25$, $\tau_0 = 5. \times 10^{-9}$ s/rad, $\tau_2 = 1. \times 10^{-9}$ s/rad.

is neglected.

The effect is clearly more important at high orders, since then the anisotropy in $\tilde{A}$ is the largest. The problem of the influence that the non-quantization effect has on the correlation times, and on $\bar{P}_4$ extracted by analysing experimental angular dependent linewidth coefficients is now under investigation.

CHAPTER SEVEN

SPIN RELAXATION FOR BIRADICAL SPIN PROBES IN ANISOTROPIC ENVIRONMENTS

7.1 Introduction

The large zero-field splitting of certain biradicals makes them important candidates for spin probes of anisotropic systems such as liquid crystals and membranes. The electron resonance spectrum of a biradical dissolved in a liquid crystal may be influenced by the zero-field splitting in two quite distinct ways. Firstly the line positions are affected because the spin probe is partially oriented by the liquid crystal solvent. In addition the zero-field splitting coupled with the molecular reorientation constitutes a powerful spin relaxation process and so may determine the width of the spectral lines. Here we develop a theory of such line broadening, within the limit of fast motion, and show how it results in an angular dependence of the linewidths. The application of the theory is illustrated by studying the line broadening for a nitroxide biradical dissolved in a nematic mesophase. An analysis of the angular dependence of the linewidths suggests that the diffusion model provides a better account of molecular reorientation in a liquid crystal than the strong-collision approach. Finally we draw attention to the potential value of the theory for understanding the linewidth variations in the deuteron magnetic resonance spectra of liquid crystals.

7.2 (a) Theory

The majority of stable biradicals are formed by linking two nitroxide groups together; consequently the dominant magnetic interactions are the zero-field splitting together with the Zeeman and nitrogen hyperfine couplings. However, in developing the theory, we shall find it convenient to ignore all hyperfine interactions and such an assumption will be permissible provided the zero-field splitting exceeds the hyperfine interaction. In situations where the hyperfine terms are important it would be a straight forward matter to extend the present theory although the book-keeping could become somewhat involved (152). We begin by obtaining the static spin hamiltonian for a biradical in an anisotropic environment and then proceed to the spin relaxation problem.

7.2 (b) Statics

The spin hamiltonian for a given orientation of a biradical may be written, in irreducible spherical tensor notation (34), as

$$H = H^0 + \sum_p (-1)^p D^{(2,p)} T^{(2,-p)}, \quad (7.1)$$

where H^0 contains the orientation independent Zeeman and exchange interactions. In the second term, $D^{(2,p)}$ is the p th component of the zero-field splitting tensor and $T^{(2,-p)}$ is the appropriate combination of total electron spin operators. We list the components of the spatial and spin operators, which we use, in Table 7.1 because various definitions are encountered in the literature.

TABLE 7.1 The irreducible spherical tensor components

p	$D^{(2,p)}$	$T^{(2,p)}$
0	$(3/2)^{1/2} D_{zz}$	$(2/3)^{1/2} \{ S_z^2 - (1/4) (S_+ S_- + S_- S_+) \}$
± 1	$\mp (D_{xz} \pm i D_{yz})$	$\mp (1/2) (S_{\pm} S_z + S_z S_{\pm})$
± 2	$(1/2) (D_{xx} - D_{yy} \pm 2i D_{xy})$	$(1/2) S_{\pm}^2$

This spin hamiltonian is written in a molecular co-ordinate system and so the spin operators fluctuate in time as the molecule reorients; it is this motion which combines with the zero-field splitting to yield the spin relaxation process. The time dependence may be removed from the spin operators by transforming to a space fixed co-ordinate system which we choose to contain the symmetry axes of the ordering potential responsible for the partial alignment of the spin probe.

This gives

$$H(t) = H^0 + \sum_{p,q} (-1)^p D^{(2,p)} T^{(2,q)} D_{q,-p}^2(t) \quad (7.2)$$

where $D_{q,-p}^2(t)$ is a second rank Wigner rotation matrix which contains the complete time dependence of the spin hamiltonian. The molecular motion is assumed to be sufficiently fast that the static spin hamiltonian may be obtained by taking a time or ensemble average of equation (7.2). In other words the relevant rotational correlation times are smaller than the inverse of the zero-field splitting. We therefore require the average $\overline{D_{q,-p}^2}$ and for an environment with $D_{\infty h}$

symmetry, such as a nematic or smectic A liquid crystal, this quantity vanishes unless q is zero. The static spin hamiltonian is then

$$\bar{H} = H^0 + \tilde{D}^{(2,0)} T^{(2,0)}, \quad (7.3)$$

where the partially averaged zero-field splitting is defined by

$$\tilde{D}^{(2,0)} = \sum_p (-1)^p D^{(2,p)} \overline{D_{0,-p}^2}, \quad (7.4)$$

and $\overline{D_{0,-p}^2}$ is a measure of the alignment of the spin probe by its environment. This spin hamiltonian corresponds to a triplet state with a cylindrically symmetric zero-field splitting tensor and the magnetic behaviour of such a system is completely understood (115). When the magnetic field is parallel to the symmetry axis of D the three triplet spin functions $|1\rangle$, $|0\rangle$ and $|-1\rangle$ are eigenfunctions of $\bar{H}$. For all other orientations of the sample these spin states are mixed by the zero-field splitting; however, provided D is small in comparison with the Zeeman splitting, then the triplet functions are good approximations to the eigenfunctions. Within this high-field approximation the two allowed transitions are

$$|0\rangle \leftrightarrow |1\rangle \equiv |+\rangle,$$

and (7.5)

$$|-1\rangle \leftrightarrow |0\rangle \equiv |-\rangle.$$

The electron resonance spectrum therefore contains two lines with resonant fields

$$B_{\pm} = \frac{\hbar\omega_0}{g\beta} \pm \frac{3\tilde{D}_{||}}{2g\beta} P_2(\cos\gamma), \quad (7.6)$$

where $\tilde{D}_{||}$ is the cartesian component of the partially averaged zero-field splitting tensor parallel to its symmetry axis and so to the director; the angle between the magnetic field and the director is γ . The spacing between the two spectral lines changes dramatically with this angle and we shall now see that the linewidths should also exhibit a pronounced angular dependence.

7.2 (c) Dynamics

It is necessary to calculate the linewidths using the Liouville space or Binsch (112) formalism discussed in Chapter 4 because for certain orientations of the sample the separation between the two spectral components is comparable to the linewidth. Under such conditions Redfield's relaxation theory alone is unable to predict the line shape in contrast to the situation when the transitions are either degenerate or well resolved (100). Since the motion is assumed to be fast the line shape in a slow-passage, low-power electron resonance experiment is given by (c.f. Section 4.2)

$$S(\omega) \propto \text{Re}\{\tilde{S}_{-} \cdot M^{-1} \cdot S_{-}\} . \quad (7.7)$$

The vector S_{-} is composed of the matrix elements $\langle a | S_{-} | a' \rangle$ where $|a\rangle$ denotes an eigenfunction of $\bar{H}$. The matrix M is related to

Redfield's relaxation matrix R (100) and the transition frequencies by

$$M_{aa'bb'} = i(\omega_{a'a} - \omega) \delta_{ab} \delta_{a'b'} + R_{aa'bb'}. \quad (7.8)$$

For the triplet-state problem the vector S_- is proportional to (1,1). The resonant frequencies may be replaced by resonant fields because, according to equation (7.6) there is a 1:1 correspondence between magnetic field and frequency. The relaxation matrix is calculated, in the usual way, from the dynamic spin hamiltonian $H_1(t)$ which is obtained by subtracting the static spin hamiltonian from its instantaneous value $H(t)$. Thus

$$H_1(t) = \sum_{p,q} (-1)^p D^{(2,p)} \{ D_{q,-p}^2(t) - \overline{D_{0,-p}^2} \delta_{0q} \} T^{(2,q)}, \quad (7.9)$$

where $T^{(2,q)}$ depends on the orientation of the director with respect to the magnetic field. This angular dependence is removed by transforming the spin operator to a laboratory frame containing the field

$$H_1(t) = \sum_{p,q,r} (-1)^p D^{(2,p)} \{ D_{q,-p}^2(t) - \overline{D_{q,-p}^2} \delta_{0q} \} D_{r,q}^2 T^{(2,r)}, \quad (7.10)$$

which we write formally as

$$H_1(t) = \sum_r (-1)^r F^{(2,r)} T^{(2,-r)}, \quad (7.11)$$

where $F^{(2,r)}$ contains both the time and angular dependence of the dynamic perturbation. The relaxation matrix is then found to be

$$R \equiv \begin{array}{c} \begin{array}{cc} & \begin{array}{c} |+\rangle \\ |-\rangle \end{array} \\ \begin{array}{c} \langle +| \\ \langle -| \end{array} & \begin{bmatrix} A & B \\ B & A \end{bmatrix} \end{array}, \quad (7.12)$$

where the basis functions correspond to the two allowed transitions: the matrix elements are

$$A = -\left(\frac{3}{2} J_0 + \frac{3}{2} J_1 + J_2 \right), \quad (7.13)$$

and

$$B = -J_1. \quad (7.14)$$

These spectral densities are related to the Fourier transform of the correlation function for the spatial operator $F^{(2,r)}$ by

$$J_r = \frac{1}{2} \int_{-\infty}^{\infty} \overline{F^{(2,r)}(0)} F^{(2,r)*}(t) e^{-ir\omega_0 t} dt. \quad (7.15)$$

The matrix M is then

$$M \equiv \begin{bmatrix} i(\omega_0 + \delta - \omega) + A & B \\ B & i(\omega_0 - \delta - \omega) + A \end{bmatrix}, \quad (7.16)$$

within the same basis. The angular dependence of the spectrum is contained entirely within M for, as we have seen, the relaxation

matrix elements depend on the sample orientation and in addition

$$\delta = \frac{3}{2} \tilde{D}_{\parallel} P_2(\cos \gamma). \quad (7.17)$$

The general expression for the absorption spectrum is found to be

$$S(\omega) \propto -\text{Re} \left\{ \frac{A - B + i(\omega_0 - \omega)}{[A + i(\omega_0 - \omega)]^2 + \delta^2 - B^2} \right\}. \quad (7.18)$$

This adopts a particularly simple form for three limiting situations. One occurs when $\cos \gamma$ equals $1/\sqrt{3}$ for then the two transitions are degenerate and setting δ equal to zero in equation (7.18) shows that this single line has a lorentzian shape with a width

$$T_2^{-1} = -(A + B). \quad (7.19)$$

At the other extreme the two lines are well resolved and so the line separation δ is large compared with the linewidth whose magnitude is of order A . In addition inspection of equations (7.13) and (7.14) for A and B reveals that B is always less than A , consequently $\delta > B$. The off-diagonal elements in M may therefore be ignored and the spectrum calculated from equation (7.16) is found to be a sum of two lorentzians separated by δ and with equal widths:

$$T_2^{-1} = -A. \quad (7.20)$$

For intermediate situations the entire line shape should be computed from equation (7.18); fortunately this is not always necessary.

When the molecular motion is slow in the sense that the rotational correlation time is large compared with the inverse of the microwave frequency ω_0 then the non-secular spectral densities J_1 and J_2 are small in comparison with the secular contribution J_0 . Under these conditions B may be ignored in comparison with A and the line shape is lorentzian for all sample orientations with a width

$$\begin{aligned} T_2^{-1} &= -A, \\ &= \frac{3}{2} J_0. \end{aligned} \tag{7.21}$$

In the remainder of the linewidth calculation for the electron resonance spectrum of the biradical we shall take this to be the case.

The calculation demands a knowledge of the spatial operator $F^{(2,r)}$ which is obtained by a direct comparison of equations (7.10) and (7.11). This operator may then be used to evaluate the spectral density J_0 , for a particular orientation as

$$\begin{aligned} J_0 = & \sum_{\substack{p,p' \\ q,q'}} (-1)^{p+p'} D^{(2,p)} D^{(2,p')*} D_{0,q}^2 D_{0,q'}^{2*}, \\ & \frac{1}{2} \int_{-\infty}^{\infty} \{ D_{q,-p}^2(0) D_{q',-p'}^{2*}(t) - \overline{D_{0,-p}^2} \overline{D_{0,-p'}^2} \delta_{0q} \delta_{0q'} \} dt. \end{aligned} \tag{7.22}$$

The simplification of this multiple summation is entirely analogous to the procedure adopted in calculating the angular dependence of the linewidth for doublet state species (c.f. Chapter 5). There it was shown that terms in the summation vanish unless q equals q' , because the mesophase is cylindrically symmetric, and so

$$J_0 = \sum_{\substack{L; p, p' \\ q}} (-1)^{p+p'+q} D^{(2,p)} D^{(2,p')*} C(22L;00) C(22L;q-q) P_L(\cos \gamma) \quad (7.23)$$

$$\times \frac{1}{2} \int_{-\infty}^{\infty} \{ \overline{D_{q,-p}^2(0)} \overline{D_{q,-p'}^{2*}(t)} - \overline{D_{0,-p}^2} \overline{D_{0,-p'}^2} \delta_{0q} \} dt,$$

where the product of rotation matrices has been replaced with a sum of Legendre polynomials by resorting to the Clebsch-Gordan series (34). The summation is restricted to even values of L because of the $D_{\infty h}$ symmetry of the environment and so the angular dependence of the linewidth is found to be

$$T_2^{-1} = X_0 + X_2 P_2(\cos \gamma) + X_4 P_4(\cos \gamma). \quad (7.24)$$

To proceed further and obtain explicit expressions for the angular linewidth coefficients we shall require some model for the molecular reorientation process. Two quite different approaches (strong collision and diffusion) are available, although both find it particularly convenient to restrict attention to those spin probes for which the ordering tensor $\overline{D_{0,p}^2}$ is cylindrically symmetric, that is the only non-vanishing component has $p=0$. Of course the magnitude of the ordering tensor is determined by the solute-solvent interactions and we can only be certain that $\overline{D_{0,p}^2}$ is cylindrically symmetric when the spin probe has the same symmetry. In practice there are few spin probes with cylindrical symmetry although this does not guarantee that the ordering tensor for the remainder are not cylindrically symmetric, but now the symmetry must be established experimentally. Providing the ordering tensor is cylindrically symmetric we may replace $\overline{D_{0,p}^2}$, in

equation (7.23) for the spectral density J_0 by $\bar{P}_2 \delta_{0p}$ and, more importantly, we can eliminate those terms with p not equal to p' ; the expression for X_L reduces to:

$$X_L = \frac{3}{2} \sum_{p,q} (-1)^q |D^{(2,p)}|^2 C(22L;00)C(22L;q-q) j_{q-p}, \quad (7.25)$$

where the spectral density j_{q-p} is

$$j_{q-p} = \frac{1}{2} \int_{-\infty}^{\infty} \{ D_{q,-p}^2(0) D_{q,-p}^{2*}(t) - \bar{P}_2^2 \delta_{0p} \delta_{0p} \} dt. \quad (7.26)$$

The components of the zero-field splitting tensor must now be expressed in the co-ordinate system which contains the symmetry axis for the ordering tensor as one of the axes. There are several variants of the first model which is based implicitly on the notion of a strong collision which results in instantaneous molecular reorientation through any angle (c.f. the previous Chapters). If, on average, the time between reorientational collisions is τ then the correlation function, which is the integrand in equation (7.26), decays exponentially with a single time constant τ ; accordingly

$$j_{q-p} = \left\{ \sum_{L'} (-1)^{p+q} C(22L';q-q)C(22L';-pp) \bar{P}_{L'} - \bar{P}_2^2 \delta_{0p} \delta_{0q} \right\} \tau. \quad (7.27)$$

As usual we introduce correlation times dependent on the modulus of p , $\tau_p \equiv \tau_{|p|}$ instead of τ as a way to reflect the anisotropy of the molecular reorientation (52). One of the major advantages of this approach is its mathematical simplicity, for example the angular

linewidth coefficients are readily calculated to be

$$X_L = \frac{3}{2} \sum_p (-1)^p |D^{(2,p)}|^2 C(22L;00)C(22L;-pp)\{\bar{P}_L - \bar{P}_2^2 \delta_{0p}\} \tau_p. \quad (7.28)$$

Evaluation of the Clebsch-Gordan coefficients (34) then gives the explicit expressions for X_L as

$$X_0 = (3/10)\{|D^{(2,0)}|^2(1-\bar{P}_2^2)\tau_0 + 2|D^{(2,1)}|^2\tau_1 + 2|D^{(2,2)}|^2\tau_2\}, \quad (7.29)$$

$$X_2 = (3/7)\{|D^{(2,0)}|^2(\bar{P}_2 - \bar{P}_2^2)\tau_0 + |D^{(2,1)}|^2\bar{P}_2\tau_1 - 2|D^{(2,2)}|^2\bar{P}_2\tau_2\}, \quad (7.30)$$

and

$$X_4 = (9/35)\{3|D^{(2,0)}|^2(\bar{P}_4 - \bar{P}_2^2)\tau_0 - 4|D^{(2,1)}|^2\bar{P}_4\tau_1 + |D^{(2,2)}|^2\bar{P}_4\tau_2\}. \quad (7.31)$$

The linewidth coefficients thus depend on the three correlation times τ_0, τ_1, τ_2 . To reduce the number of parameters we make the further assumption that

$$\tau_p^{-1} = \tau_0^{-1} \{4 + (\tau_0 \tau_2^{-1} - 1)p^2\} \quad (7.32)$$

This relation provides a sort of interpolation for τ_1 in terms of τ_0 and τ_2 and it is suggested by the comparison e.g. with the well know expressions for the correlation times for rotational diffusion in an isotropic system (126). Of course the validity of the assumption can only be justified by comparison with experiment and at present the few results available seem to support these intuitive expression for the

spectral densities in anisotropic systems.

As we mentioned in the Introduction, electron spin relaxation for a triplet state is identical to nuclear spin relaxation, for a nucleus of spin 1, by the quadrupole interaction (153). Consequently a partial check of equations (7.29-7.31) is possible because Egozy et al (154) have calculated the deuterium relaxation times, T_1 and T_2 , for perdeuterated benzene dissolved in a nematic mesophase. However, they restrict their attention to the situation when the director is parallel to the magnetic field, the field gradient at the deuterium nucleus is cylindrical symmetric and the molecular reorientation can be described by a single correlation time, as in the simple version of the strong collisional model. If we impose all of these restrictions on equations (7.24) and (7.29-7.31) then we obtain the secular contribution to the linewidth, T_2^{-1} , which has the same form as that found by Egozy et al but which is twice as large. Since our results yield the correct limiting value for the secular part of T_2^{-1} when both the system and the motion is isotropic (153) we suppose their equation is error. At the other extreme the molecular reorientation is assumed to proceed via small angle jumps, that is according to the diffusion model discussed in Section 4.4 (b). According to this model the spectral densities at zero frequency are given by (96)

$$j_{qp} = \sum_{\substack{L' \neq 0 \\ L''(\text{even})}} \{ (-1)^{p+q} C(2L'L''; q-q) C(2L'L''; p-p) \bar{P}_{L''} - \bar{P}_2 \bar{P}_{L'} \delta_{0p} \delta_{0q} \} \tau_{L', q, p}$$

(7.33)

The time constants $\tau_{L,qp}$ depend on the components of the probe diffusion tensor and on the orientational order; they have been defined in terms of the Nordio et al (96) R^{qp} matrix in Section 4.4 (d).

The diffusion tensor D is assumed to be cylindrically symmetric and its symmetry axis to be coincident with that of the ordering tensor.

An explicit expression for the linewidth coefficients can be obtained, remembering the symmetry rules

$$j_{qp} = j_{-q-p} = j_{q-p} = j_{-qp} ,$$

as

$$x_0 = (3/10) \{ |D^{(2,0)}|^2 (j_{00} + 2j_{10} + 2j_{20}) + 2 |D^{(2,1)}|^2 (j_{01} + 2j_{11} + 2j_{21}) + 2 |D^{(2,2)}|^2 (j_{02} + 2j_{12} + 2j_{22}) \} , \quad (7.34)$$

$$x_2 = (3/7) \{ |D^{(2,0)}|^2 (j_{00} + j_{10} - 2j_{20}) + 2 |D^{(2,1)}|^2 (j_{01} + j_{11} - 2j_{21}) + 2 |D^{(2,2)}|^2 (j_{02} + j_{12} - 2j_{22}) \} , \quad (7.35)$$

and

$$x_4 = (9/35) \{ |D^{(2,0)}|^2 (3j_{00} - 4j_{10} + j_{20}) + 2 |D^{(2,1)}|^2 (3j_{01} - 4j_{11} + j_{21}) + 2 |D^{(2,2)}|^2 (3j_{02} - 4j_{12} + j_{22}) \} . \quad (7.36)$$

In the following section we shall compare the predictions of the two dynamical models with the angular linewidth coefficients measured for a nitroxide biradical dissolved in a nematic mesophase.

7.3 (a) The Experiment

The biradical spin probe employed to test the theoretical predictions was 1,4-bis(3-spiro-[2'-N-oxyl-3',3'-dimethyloxazolidine]) cyclohexane which has the structure shown in figure 7.1. The spin probe was synthesised from cyclohexan-1,4-dione using the route described by Michon and Rassat (155). The nematogen, 4,4'-di-n-butyloxyazoxybenzene, was purchased from Eastman Kodak Ltd, and purified by recrystallisation from ethanol (T_{S-N} 102°C; T_{N-I} 132°C). In the experiment the orientation of the director is controlled by an electric field, consequently the sample, made by doping the nematogen with the spin probe, was contained in a cell made from two glass plates approximately 1cm×10cm and held 125 μ apart with a Teflon spacer. The inner surfaces of the plates were coated with tin oxide and this allows the application of an electric field perpendicular to the surface. In the absence of an electric field the director is aligned parallel to the spectrometer's magnetic field, however the magnetic forces responsible for this alignment are overcome by a 14 kHz electric field from an applied voltage of 90 volts. Under these conditions the director is aligned perpendicular to the electric field and so parallel to the plates of the cell because the anisotropic permittivity is negative (39). The only effect of the magnetic field now is to constrain the director to lie in the plane containing both the magnetic and electric fields. The angle γ between the director and the magnetic field is then 90° minus the angle made by the electric field with the magnetic field. The cell was mounted in a goniometer and the angular dependence of the spectrum for the spin probe in the nematic mesophase was recorded; the measurements were made at two temperatures, 127°C and 104°C.

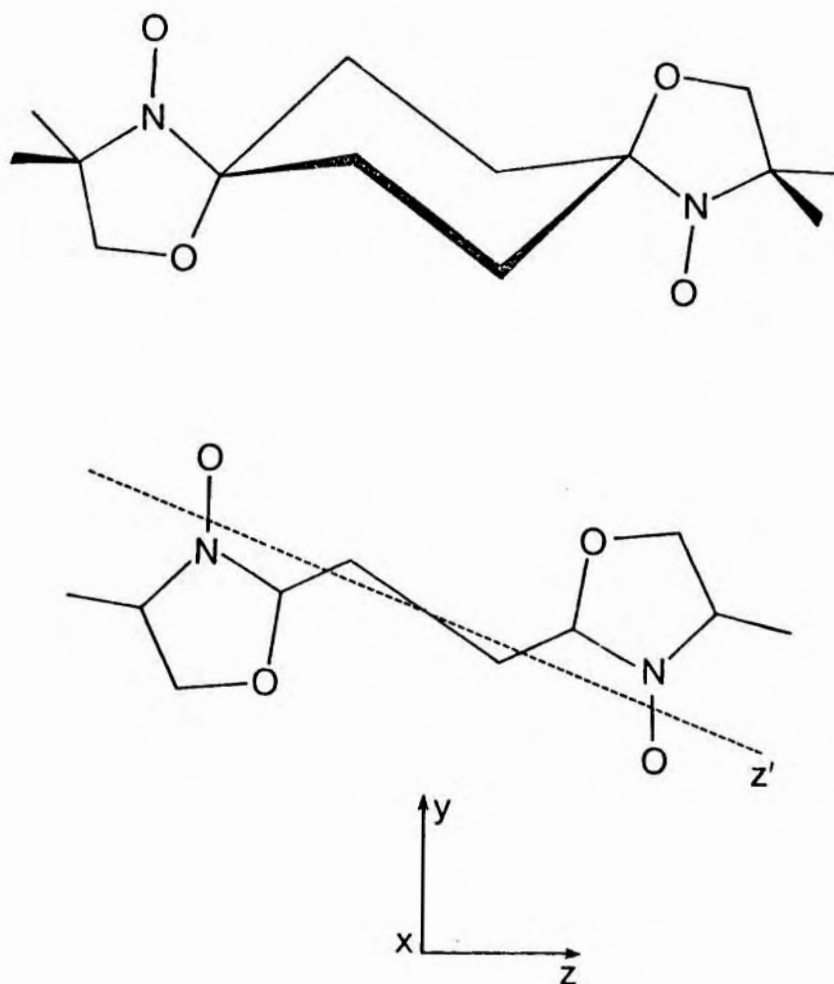


Figure 7.1 The molecular structure of the biradical spin probe 1,4-bis(3-spiro-[2' N-oxyl-3',3'-dimethoxazolidine]) cyclohexane together with a co-ordinate system in which the ordering tensor is supposed to be cylindrically symmetric.

Typical spectra are shown in figure 7.2 for the sample at 104°C with the director parallel and perpendicular to the magnetic field, these two spectra clearly demonstrate the angular dependence of the linewidth and we shall now describe the determination of these widths.

7.3 (b) Spectral Analysis

The spectra in figure 7.2 are dominated by the dipolar splitting whose angular dependence is predicted by equation (7.6); for those orientations where the dipolar splitting is well resolved there is complete agreement between the observed and theoretical line separations. The values of $\tilde{D}_{||}$ determined from the angular dependence for the two temperatures are given in Table 7.2. The spectrum, for the

TABLE 7.2 The partially averaged magnetic parameters

Temperature (°C)	$\tilde{D}_{ }$ (MHz)	$\tilde{A}_{ }$ (MHz)	$\tilde{A}_{\perp}$ (MHz)	$\tilde{D}_{ } / (\tilde{A}_{ } - \tilde{A}_{\perp})$
104°	101	29.2	47.2	-5.6
127°	64	33.7	44.9	-5.7

director orthogonal to the magnetic field, also exhibits hyperfine structure from the two equivalent nitrogen nuclei, the spacing between the lines is just one half the nitrogen coupling constant because the electron-electron interaction greatly exceeds the hyperfine interaction (156). For many orientations the hyperfine splitting is not resolved but does result in inhomogeneous broadening of the spectral

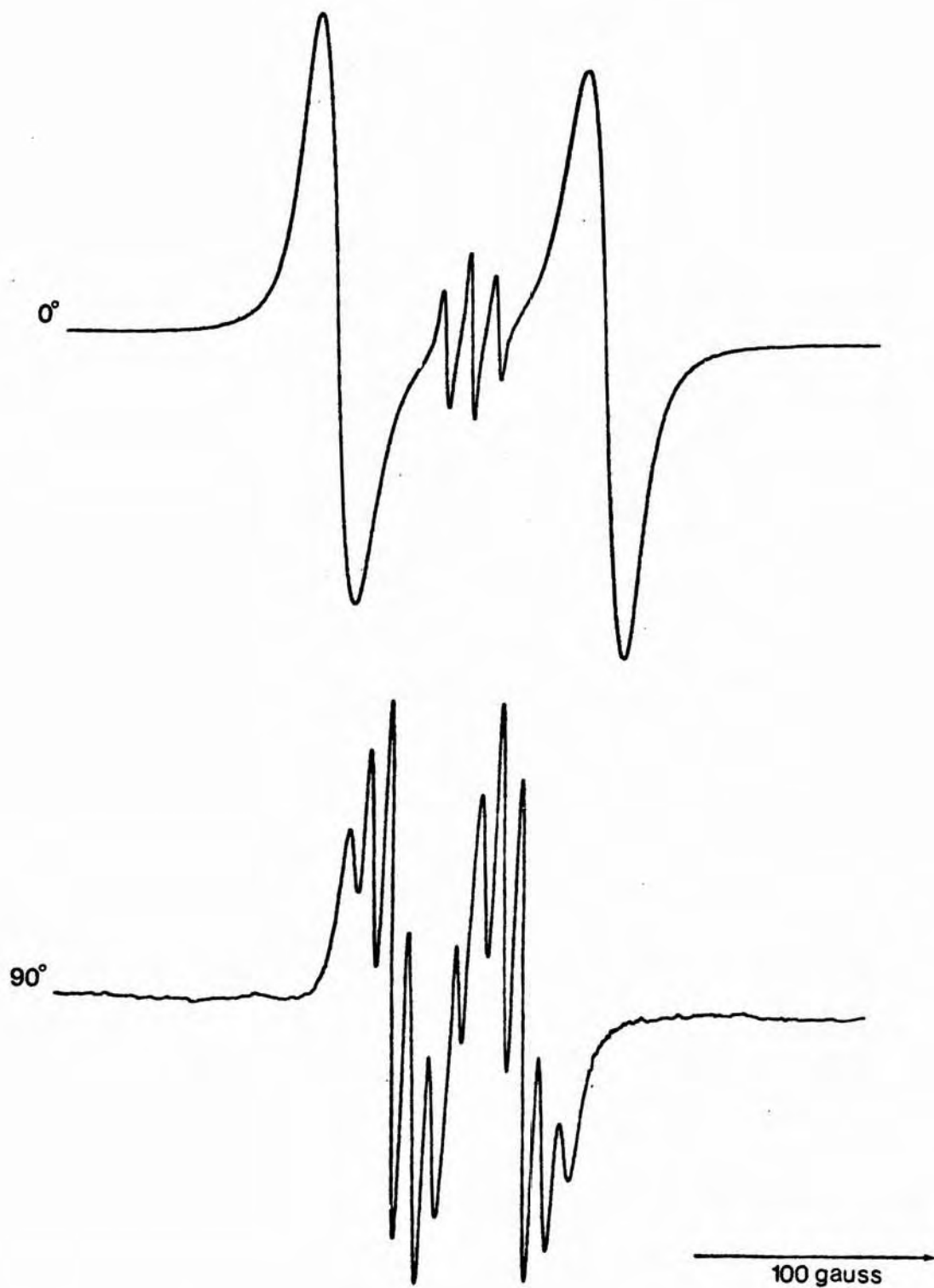


Figure 7.2 The electron resonance spectrum of the biradical in the nematic mesophase of 4,4'-di-n-butyloxyazoxybenzene at 104°C with the director (a) parallel and (b) perpendicular to the magnetic field.

lines, consequently it is essential to allow for this broadening when obtaining the true linewidth. We have therefore simulated spectra which incorporate both the dipolar and hyperfine splittings, the linewidth was then varied until agreement with the observed spectrum was obtained. The angular dependence of the coupling constant, required in the simulations, is given by (39)

$$\bar{a}(\gamma) = \{\tilde{A}_{\parallel}^2 \cos^2\gamma + \tilde{A}_{\perp}^2 \sin^2\gamma\}^{\frac{1}{2}}, \quad (7.37)$$

since the anisotropy in the partially averaged g tensor is negligibly small. The values of the two components of the partially averaged nitrogen hyperfine tensor employed in the spectral simulations are given in Table 7.2. Since $\bar{a}(\gamma)$ could not always be obtained from the spectrum of the biradical we have also measured the nitrogen coupling constant of the nitroxide monoradical, which is responsible for the central three lines in figure 7.2a. The radical is almost certainly the hydroxylamine derivative of the biradical formed by hydrogen abstraction from the solvent. In view of the great similarity of the structures of mono and biradical we expect their partially averaged nitrogen hyperfine tensors to be the same and this is found to be so when both splittings can be measured simultaneously. The linewidths obtained by matching the theoretical and experimental spectra are plotted against the director orientation in figure 7.3 for the sample at 104°C; a similar angular dependence was observed at 127°C.

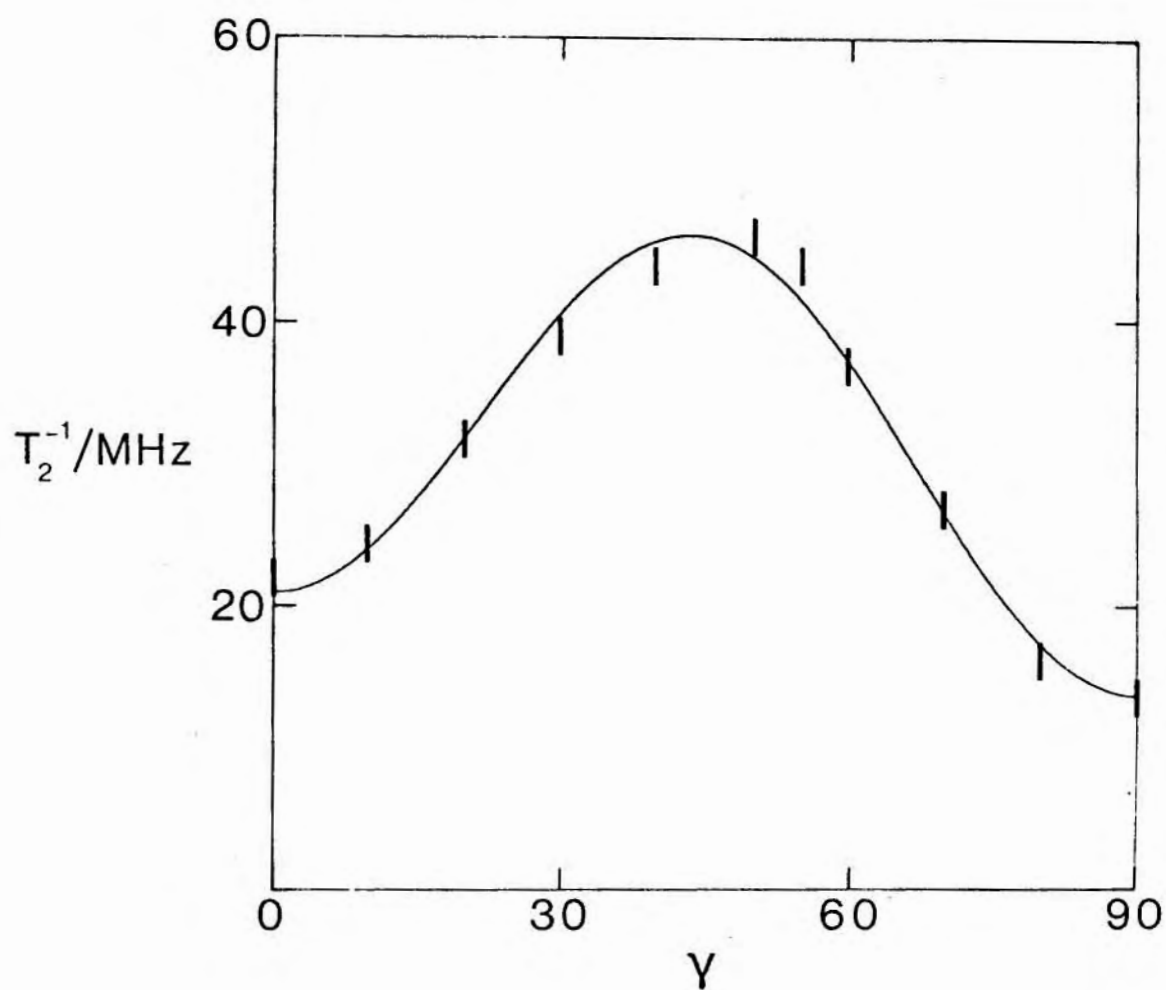


Figure 7.3 The angular dependence of the linewidth for the biradical dissolved in the nematic mesophase at 104°C. The solid line is the best fit to equation (7.25).

7.3 (c) The Molecular Symmetry

The expressions obtained for the angular linewidth coefficients are only valid when the ordering tensor $\overline{D_{0,p}^2}$ for the spin probe is cylindrically symmetric. The spin probe employed in the experiments does not possess cylindrical symmetry and so we must first show that $\overline{D_{0,0}^2}$ is the only non-zero component of the ordering tensor. There are five unknown order parameters and since there are only two independent pieces of experimental information ($\tilde{A}_{||}$ and $\tilde{D}_{||}$) all we can hope to achieve is to show that they are consistent with an assumed cylindrical symmetry. The spin probe may exist in one of several conformations but solid-state electron resonance studies indicate that the equatorial-equatorial chair form of the trans isomer, shown in figure 7.1, is preferred (157). Examination of molecular models then suggests that the ordering tensor for the spin probe in the nematic mesophase should be cylindrically symmetric about the z axis shown in figure 7.1, together with a projection formula for the conformer. Provided the assumption of cylindrical symmetry is correct then the components of the partially averaged tensors are given by

$$\tilde{D}_{||} = (2/3)^{\frac{1}{2}} D^{(2,0)} \overline{P}_2, \quad (7.38)$$

and

$$\tilde{A}_{||} - \tilde{A}_{\perp} = (3/2)^{\frac{1}{2}} A^{(2,0)} \overline{P}_2, \quad (7.39)$$

where the zeroth component of the appropriate anisotropic tensor is evaluated in the xyz co-ordinate system, shown in figure 7.1. The nitrogen hyperfine tensor, for such oxazolidines, is cylindrically

symmetric about the x axis (157) and so

$$A^{(2,0)} = -(3/8)^{\frac{1}{2}} A'_{\parallel} \quad (7.40)$$

where $A'_{\parallel}$ is the component of the anisotropic tensor along this symmetry axis. The zero-field splitting tensor is, to a good approximation, also cylindrically symmetric (155,157) but about the z' axis which makes an angle θ with the z axis and so

$$D^{(2,0)} = (3/2)^{\frac{1}{2}} \frac{(3 \cos^2 \theta - 1)}{2} D_{z'z'} \quad (7.41)$$

Because the symmetry axes of the two magnetic tensors are not parallel the ratio $\tilde{D}_{\parallel} / (\tilde{A}_{\parallel} - \tilde{A}_{\perp})$ may only be independent of temperature if the ordering tensor is cylindrically symmetric. The values calculated for this ratio are essentially constant as we can see from the results given in Table 7.2. The angle θ can be extracted from these values for $\tilde{D}_{\parallel} / (\tilde{A}_{\parallel} - \tilde{A}_{\perp})$ since, from equations (7.38-7.41)

$$\frac{(3 \cos^2 \theta - 1)}{2} = - \frac{3 \tilde{D}_{\parallel}}{4 (\tilde{A}_{\parallel} - \tilde{A}_{\perp})} \frac{A'_{\parallel}}{D_{z'z'}} \quad (7.42)$$

Calculation of θ provides us with an additional check on the assumption of cylindrical symmetry because this angle may be estimated from molecular models. Thus the z' axis has been found to intersect the N-O bonds at about one quarter of the bond length from nitrogen (157) and so θ should be about 20° , given our assignment of the z axis. Since θ is relatively small rather precise values of the parameters occurring in equation (7.42) are required to obtain a reliable estimate

of this angle. The zero-field splitting tensor is known, with some accuracy, from single crystal studies and $D_{z'z'}$ is found to be 230 MHz (157). Unfortunately the anisotropic hyperfine tensor is not known with such certainty and three reasonable values are available. The single crystal study of the biradical yields a value for $A'_{\parallel}$ of 52.5 MHz although the accuracy is said not to be high (157). A more reliable value of 51.1 MHz has been determined for the structurally related monoradical 2-N-oxyl,1,1,3,3,-tetramethyloxazolidine (157). Finally $A'_{\parallel}$ is 48.7 MHz for another monoradical, (3-spiro-[2'-N-oxyl-3',3'-dimethyloxazolidine])-5 α -androstand-17 β -ol (158), which, in view of the cyclic groups, should be most closely related to the biradical. The magnitudes of θ and $\bar{P}_2$ obtained from the single value of $D_{z'z'}$, together with these three values of A' are listed in Table 7.3 for both temperatures. The angle θ is seen to range from 8° to 15° even though the component of the anisotropic hyperfine tensor only changes by an amount, 3.8 MHz, not greatly in excess of the experimental error in $A'_{\parallel}$.

TABLE 7.3 The derived parameters θ and $\bar{P}_2$

$A'_{\parallel}$ /MHz	Temperature (°C)			
	104°		127°	
	θ	$\bar{P}_2$	θ	$\bar{P}_2$
52.5	9°	0.46	8°	0.29
51.1	12°	0.47	11°	0.29
48.7	15°	0.49	15°	0.31

In view of this extreme sensitivity of the angle to $A'_{\parallel}$ we believe the results for θ are also in accord with the assumption of a cylindrically symmetric ordering tensor. In addition we shall take θ to be 15° in subsequent calculations because this value is closest to our original estimate of 20° based on an examination of molecular models.

7.3 (d) The Angular Linewidth Coefficients

As we have just seen our assumption of a cylindrically symmetric ordering tensor is not unreasonable and so we may now turn to a detailed analysis of the linewidths. The first test of the theory is to see if the angular dependence of the linewidths is in accord with that predicted by equation (7.24). The theoretical angular dependence of T_2^{-1} is shown as the solid line in figure 7.3 and is seen to be in good agreement with experiment; comparable agreement is also found for the linewidths measured at 127°C . Of course such comparisons do not provide a particularly severe test for the theory because the predicted angular dependence of the linewidth stems directly from the $D_{\infty h}$ symmetry of the anisotropic environment and the second rank nature of the zero-field splitting tensor. In fact the good agreement between theory and experiment may be taken as confirmation of our correct assignment of the dominant spin relaxation process. A more searching test of the theory is provided by an attempt to predict the observed angular linewidth coefficients X_L ; these are listed in Table 7.4 and were obtained by fitting equation (7.24) for $T_2^{-1}(\gamma)$ to the experimental linewidths. There are, of course, two theoretical expressions for the coefficients X_L and one of the major objectives of any experimental linewidth

TABLE 7.4 The angular linewidth coefficients

Temperature (°C)	X_0 (MHz)	X_2 (MHz)	X_4 (MHz)	X_0/X_2	X_0/X_4
104°	31.4±0.5	16±1	-26±1	2.0±0.2	-1.21±0.07
127°	29.5±0.9	9±2	-14±2	3.3±0.8	-2.1 ±0.4

investigation is to distinguish between the two extreme models for molecular reorientation. However in this study we shall be primarily concerned with using the experimental results, which are not of high accuracy, simply to illustrate the theory.

We now proceed to calculate the angular linewidth coefficients using both models. To make the comparison with experiment as equitable as possible the ordering potential, given in general by a sum of even Legendre polynomials (c.f. Chapter 2), will be restricted to just the first term, i.e.

$$\frac{U}{kT} = \lambda_2 P_2(\cos\beta), \quad (7.43)$$

in both calculations. The magnitude of the single parameter λ_2 may then be calculated from the observed value of the order parameter $\bar{P}_2$; the results of this calculation are in Table 7.5. Because the potential is restricted to a single term both dynamic models lead to sets of equations for X_L which contain just two arbitrary parameters. In addition the ratios X_0/X_2 and X_0/X_4 of the angular linewidth coefficients

TABLE 7.5 The order parameters

Temperature (°C)	$\bar{P}_2$	$\bar{P}_4$	λ_2
104°	0.49	0.16	-2.3
127°	0.31	0.06	-1.4

are seen to depend on the ratio of the appropriate parameters; in the case of the strong collision model this is τ_0/τ_2 while for the diffusion model it is $D_{\parallel}/D_{\perp}$.

We begin with the strong collision model; the evaluation of the linewidth coefficients requires the order parameter $\bar{P}_4$ and this was calculated from the values for λ_2 with the results given in Table 7.5. This procedure contrasts with previous linewidth studies employing doublet states where the angular linewidth coefficients were employed to determine $\bar{P}_4$ (52-54). The components of the zero-field splitting tensor in the principal co-ordinate system, xyz, for the ordering tensor were found to be

$$\left. \begin{aligned} D^{(2,0)} &= 252 \text{ MHz,} \\ D^{(2,\pm 1)} &= 85 \text{ MHz,} \\ D^{(2,\pm 2)} &= 12 \text{ MHz.} \end{aligned} \right\} \quad (7.44)$$

and

The two ratios of the linewidth coefficients, X_0/X_2 and X_0/X_4 , were calculated from equations (7.29-7.31) for a wide range of values of the relative correlation time τ_0/τ_2 in an attempt to find agreement with experiment. However both X_0/X_2 and X_0/X_4 proved to be virtually

independent of τ_0/τ_2 and it was not possible to fit the experimental results. For example at 104°C, where the experimental data is most reliable, X_0/X_2 was predicted to change only from 2.3 to 2.2 when τ_0/τ_2 was varied from 1 to 8. This prediction is in reasonable agreement with experiment, but, in marked contrast, X_0/X_4 is calculated to be -3.7 which is over three times the observed value. It is, of course, possible to force agreement with the experimental value of X_0/X_4 by changing the magnitude of the order parameter $\bar{P}_4$, since this affects just the X_4 angular linewidth coefficient. Agreement can only be achieved when $\bar{P}_4$ is virtually zero; a result which is in accord with small values of $\bar{P}_4$ determined by Raman studies (51). However we suspect that the value is unreasonably small in view of the success of the single parameter potential in linewidth investigations employing doublet state spin probes (52-54). The analysis of the angular linewidth coefficients obtained for the biradical at 127°C yielded similar discrepancies between theory and experiment.

The angular linewidth coefficients were also evaluated using the diffusion model; again the ordering potential was restricted to a single term λ_2 taking the values given in Table 7.5. For these relatively low values of λ_2 it was found to be adequate to truncate the series expansion of the spectral density in equation (7.33) after $L''=20$. The relative linewidth coefficients were obtained for various values of $D_{||}/D_{\perp}$ and although the results were not particularly sensitive to $D_{||}/D_{\perp}$ it did prove possible to obtain the ratios X_0/X_2 and X_0/X_4 in fair, but not complete, agreement with experiment. The best fit was found for a range of values for $D_{||}/D_{\perp}$ and these are

listed in Table 7.6, together with the predicted linewidth ratios.

TABLE 7.6 The diffusion model predictions

Temperature (°C)	$D_{ }/D_{\perp}$	X_0/X_2	X_0/X_4	$D_{\perp}$ (Mrads ⁻¹)
104°	1.2	1.8	-1.4	600
	1.4	1.8	-1.5	520
	1.6	1.8	-1.6	540
127°	1.2	2.3	-3.4	720
	1.4	2.3	-3.6	700
	1.6	2.3	-3.8	680

As we expect the agreement between theory and experiment is best for the more accurate angular linewidth coefficients measured at 104°C. The agreement for the less accurate results at 127° is not so impressive although still an improvement on the predictions of the strong collisional model. The ratio $D_{||}/D_{\perp}$ for the components of the diffusion tensor is independent of temperature as we might anticipate (53). We can estimate this ratio in the hydrodynamic limit if the molecular dimensions are known (see Section 5.5); using molecular models we gauge the major semi axis to be 12 Å while the minor semi axis is about 4.5 Å. The hydrodynamic value of $D_{||}/D_{\perp}$ is then found to be 2.7, which is about twice as large as the experimental value. It is surprising to find a value below the hydrodynamic limit because similar studies of doublet-state probes have yielded value in excess of this

limit (53,128,141). Indeed, for these systems it proved necessary to introduce an anisotropic interaction tensor κ (53) whose magnitude is related to the anisotropy in the intermolecular potential (146) to account for the deviations from the hydrodynamic limit. Of course analogous explanations cannot be invoked, for rod-like molecules, when the ratio $D_{||}/D_{\perp}$ is less than the hydrodynamic limit (53).

The diffusion model of molecular reorientation in an anisotropic medium provides an adequate description of the angular linewidth coefficients, even though the ordering potential is restricted to a single term. This limited success contrasts with the apparent failure of the strong collision model which is only able to predict the ratio X_0/X_2 when the ordering potential contains a single term. In the anisotropic system which we have studied the molecular reorientation would appear to occur via rotational diffusion although more results will be required before we can differentiate with complete certainty between the two models.

7.4 Additional Spectral Features

When the director is orthogonal to the magnetic field the five nitrogen hyperfine lines associated with either component of the dipolar doublet are well resolved. Close inspection of the appropriate spectrum, shown in figure 7.2, reveals a minor variation in the widths of the hyperfine lines. Such asymmetric line broadening cannot be accounted for by the theory which we have just developed because the anisotropic hyperfine interaction was specifically excluded from the dynamic perturbation. However quite straightforward arguments (159)

show that this line broadening can be explained by inclusion of the hyperfine term in $H_1(t)$, the asymmetric linewidth effect then originates from the cross term between the anisotropic hyperfine interaction and the zero-field splitting tensor. We do not feel impelled to make detailed analysis because this broadening is quite secondary to the other linewidth variation which we have observed.

The spectral line shape is expected to be symmetric about the base line but examination of the spectrum for the director parallel to the magnetic field shows that this is not the case. Similar asymmetry in the line shape has been observed for doublet state spin probes dissolved in liquid crystals and has been attributed to non-uniform alignment of the director, probably caused by thermal fluctuations (149). A slight departure from uniform alignment of the director would also be expected to produce asymmetric line shapes for biradical spin probes and we have used spectral simulations to confirm this expectation. Of course we also expect the line shape to become asymmetric when the rate of molecular rotation is comparable to the inverse of the zero-field splitting (108). Unfortunately it is difficult to devise experiments to distinguish between these two possible explanations of asymmetric line shapes. However the rate of motion may be obtained from the inverse of the diffusion tensor; from the values listed in Table 7.6 we can see that the ratio of the zero-field splitting to either component of the diffusion tensor is just less than unity. Accordingly the assumption of rapid motion should be valid for this system and the asymmetric line shape presumably originates for non-uniform alignment of the director.

7.5 Quadrupole Relaxation

The problem which we have just solved is formally identical to the calculation of the spin relaxation times, for a nucleus of spin 1, caused by a quadrupole interaction coupled to the molecular reorientation. Consequently our results could be of value in understanding the spin relaxation behaviour of nuclei, such as deuterium, when they are incorporated in molecules forming part of a liquid crystalline system. However some caution must be exercised in the application of these results. For example although the neglect of the non-secular terms in the dynamic perturbation is a good approximation for electron resonance spectroscopy such an assumption may not be valid for nuclear magnetic resonance where the operating frequency is much smaller. If the non-secular terms do have to be retained then the entire line-shape will have to be calculated from equation (7.18) and a simple analysis is only possible when the lines are well resolved or the transitions are completely degenerate. In addition our assignment of the dominant process responsible for changes in the molecular orientation may be quite irrelevant for nuclear magnetic resonance. This situation obtains because the quadrupole interaction is considerably smaller than the zero-field splitting and so the motion with respect to the director, which we have considered, is too fast to make a significant contribution to the nuclear spin relaxation times (160). However, the molecular orientation is also changed by thermal fluctuations in the director and although this motion is slow on the electron resonance time scale it is sufficiently fast to influence the relaxation

times in nuclear magnetic resonance (161). Consequently the spectral densities employed in this Chapter would be inappropriate for calculating the deuteron relaxation times; it is however straightforward to obtain the relevant spectral densities from continuum theory (161). The calculation of the spin lattice relaxation time T_1 also presents certain difficulties especially when the two transitions are nearly degenerate. Indeed the general angular dependence of T_1 is complicated even when the spectral lines are well resolved and we shall not discuss this aspect of the problem here.

APPENDIX 1

IRREDUCIBLE TENSORS AND WIGNER ROTATION MATRICES

A tensor of rank n is a quantity that transforms under rotation as the n^{th} direct power of a vector. The 3^n dimensional representation of the rotation group realized in this way can be decomposed in a set of irreducible representations $D^{(L)}$ each of dimension $(2L+1)$. If we describe the rotations in terms of Euler angles $(\alpha\beta\gamma)$ then the matrix elements of the irreducible representation in a basis where J^2 , J_z (i.e. the angular momentum and its projection) are diagonal are (34)

$$D_{m,n}^L(\alpha\beta\gamma) = \langle Lm | e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z} | Ln \rangle. \quad (\text{A1.1})$$

The matrix elements $D_{m,n}^L(\alpha\beta\gamma)$ are called Wigner rotation matrices or Wigner functions or generalized spherical harmonics. Combinations of ordinary tensor components transforming according to the representation $D^{(L)}$ are called irreducible tensor components of rank L : $T^{(L,m)}$

$$\text{e.g.} \quad T^{(L,m)'} = \sum_n D_{n,m}^L(\Omega) T^{(L,n)} \quad (\text{A1.2})$$

Equation (A1.2) illustrates the main reason of the usefulness of irreducible tensors in problems involving rotations i.e. that their transformation properties are very simple. The set of $(2L+1)$ components, $T^{(L)}$, is called an irreducible tensor of rank L . The Euler angles $\Omega \equiv (\alpha\beta\gamma)$ in equation (A1.2) determine the rotations which carry the original (unprimed) coordinate system into the rotated (primed)

one. We follow the convention of Rose (34) for the Euler angles,

which is illustrated in figure A1.1. From equation (A1.1) it is apparent that we can express $D_{m,n}^L(\alpha\beta\gamma)$ as (34)

$$D_{m,n}^L(\alpha\beta\gamma) = e^{-im\alpha} d_{m,n}^L(\beta) e^{-in\gamma} \quad (A1.3)$$

where the real quantities

$$d_{m,n}^L(\beta) \equiv \langle Lm | e^{-i\beta J_y} | Ln \rangle \quad (A1.4)$$

are called reduced Wigner matrices.

The functions $D_{m,n}^L(\alpha\beta\gamma)$ constitute a complete orthogonal set spanning the space of the angles α, β, γ . Some of their properties, which we use most often in this thesis, are:

1. Orthogonality

$$\int D_{m,n}^{L*}(\alpha\beta\gamma) D_{m',n'}^{L'}(\alpha\beta\gamma) d\alpha \sin\beta d\beta d\gamma = \frac{8\pi^2}{2L+1} \delta_{m,m'} \delta_{n,n'} \delta_{L,L'} \quad (A1.5)$$

2. Integral of three Wigner rotation matrices

$$\begin{aligned} \int D_{m'',n''}^{L''*}(\alpha\beta\gamma) D_{m',n'}^{L'}(\alpha\beta\gamma) D_{m,n}^L(\alpha\beta\gamma) d\alpha \sin\beta d\beta d\gamma \\ = \frac{8\pi^2}{2L''+1} \delta_{m+m',m''} \delta_{n+n',n''} C(LL'L'';mm') C(LL'L'';nn') \end{aligned} \quad (A1.6)$$

where $C(abc;de)$ is a Clebsch-Gordan coefficient (34).

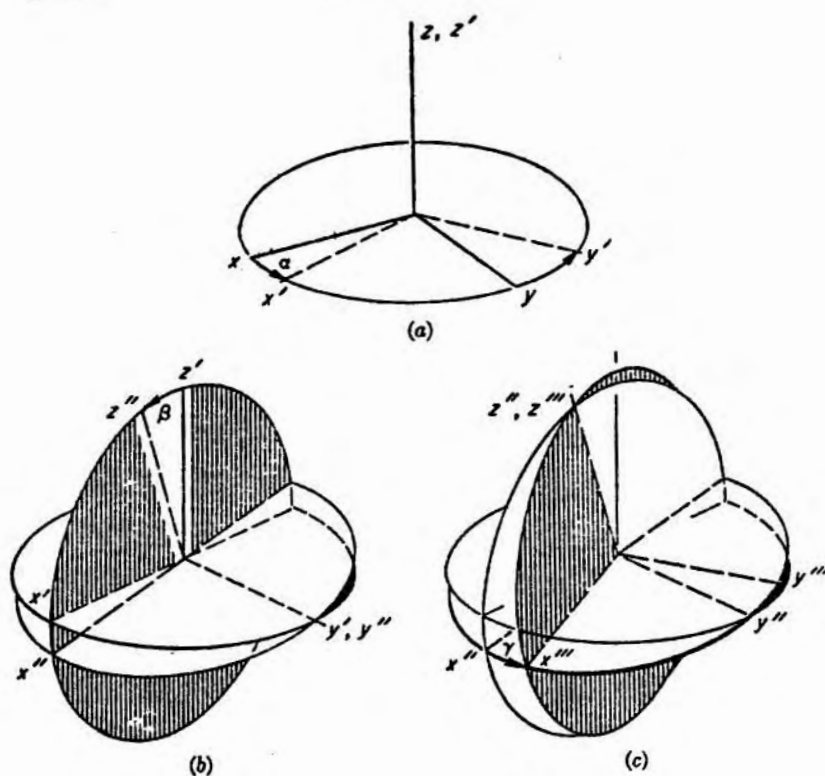


Figure A1.1 The Euler angles α , β and γ and the three Euler rotations which carry the initial (x, y, z) coordinate system into the final (x''', y''', z''') coordinate system (34).

3. Closure

$$\sum_n D_{m,n}^L(\alpha_1 \beta_1 \gamma_1) D_{n,m'}^L(\alpha_2 \beta_2 \gamma_2) = D_{m,m'}^L(\alpha \beta \gamma), \quad (A1.7)$$

where $(\alpha \beta \gamma)$ is the resultant of $(\alpha_1 \beta_1 \gamma_1)$ then $(\alpha_2 \beta_2 \gamma_2)$.

4. Symmetry

$$D_{m,n}^{L*}(\alpha \beta \gamma) = (-)^{m-n} D_{-m,-n}^L(\alpha \beta \gamma) = D_{n,m}^L(-\gamma - \beta - \alpha). \quad (A1.8)$$

5. Products

$$D_{m',n'}^{L'} D_{m'',n''}^{L''} = \sum_{L=|L'-L''|}^{L'+L''} C(L'L''L; m'm'') C(L'L''L; n'n'') D_{m'+m'', n'+n''}^L. \quad (A1.9)$$

6. Special cases

$$D_{m,0}^L(\alpha \beta 0) = \left(\frac{4\pi}{2L+1} \right)^{\frac{1}{2}} Y_{L,m}^*(\beta, \alpha), \quad (A1.10)$$

$$D_{0,0}^L(0 \beta 0) = d_{0,0}^L(\beta) = P_L(\cos \beta), \quad (A1.11)$$

where $Y_{L,m}$ is a spherical harmonic and P_L a Legendre polynomial.

APPENDIX 2

SOME PROPERTIES OF THE KUMMER CONFLUENT HYPERGEOMETRIC FUNCTIONS

We shall give here only the properties used in the text.

A thorough discussion of the confluent hypergeometric function is given in References (79,80). The Kummer function $M(a,b,z)$ can be defined as

$$M(a,b,z) = \sum_{m=0}^{\infty} \frac{(a)_m}{(b)_m} \frac{z^m}{m!}, \quad (|z| < \infty, b \neq 0, -1, -2, \dots), \quad (\text{A2.1})$$

where z, a, b , can take real and complex values and

$$(a)_m = a(a+1)\dots(a+m-1); \quad (a)_0 = 1.$$

A useful integral representation is

$$M(a,b,z) = \frac{\Gamma(b)}{\Gamma(b-a)\Gamma(a)} \int_0^1 \exp(zt) t^{a-1} (1-t)^{b-a-1} dt, \quad (\text{A2.2})$$

with $\text{Re } b > \text{Re } a > 0$.

Differentiating equation (A2.1) n times we find

$$\frac{d^n}{dz^n} M(a,b,z) = \frac{(a)_n}{(b)_n} M(a+n, b+n, z). \quad (\text{A2.3})$$

A general asymptotic expression for large arguments is

$$M(a,b,z) = \frac{\Gamma(b)}{\Gamma(a)} e^z z^{-(b-a)} \sum_{m=0}^n \frac{(b-a)_m (1-a)_m}{m!} z^{-m} + O(|z|^{-n-1}), \quad (\text{A2.4})$$

where

$$|\arg z| < \pi/2 - \delta; \quad a, b \neq 0, -1, -2, \dots$$

The Kummer functions can be expanded in a series of modified Bessel functions

$$M(a, b, z) = e^{z/2} \Gamma(b-a-1/2) (z/4)^{a-b+1/2} \times \sum_{n=0}^{\infty} \frac{(2b-2a-1)_n (b-2a)_n (b-a-1/2+n)}{n! (b)_n} (-1)^n I_{b-a-1/2+n}^{(z/2)},$$

(A2.5)

with

$$b \neq 0, -1, -2, \dots$$

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